

PATENT ABSTRACTS OF JAPAN

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(54) MAGNETIC TONER AND IMAGE FORMING METHOD

(57)Abstract:

PURPOSE: To provide a magnetic toner excellent in environmental stability and dot reproducing property, fixing property and offset resistance and capable of forming toner image having high image density even in the case of preservation for a long time.

CONSTITUTION: The magnetic toner has $\leq 13.5\mu\text{m}$ weight average particle size and $\leq 50\text{wt.\%}$ particles of $\geq 12.7\mu\text{m}$ particle size. The magnetic toner contains such iron oxide containing 0.5–4wt.% silicon element based on the iron element. The amt. (B) of silicon element present to 20wt.% of iron element dissolution of magnetic iron oxide and the amt. (A) of silicon element in the magnetic iron oxide satisfy $B/A \times 100 = 44\text{--}84\%$, and amt. (C) of silicon element on the surface of iron oxide satisfies $C/A \times 100 = 10\text{--}55\%$.

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CLAIMS**[Claim(s)]**

[Claim 1]In magnetic toner contained at least, binding resin and a magnetic oxide of iron this magnetic toner, In particle size distribution of this magnetic toner, a weight average particle size is 13.5 micrometers or less, and content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers is 50 or less % of the weight, and this magnetic oxide of iron, The content B of a silicon element in which content of a silicon element of this magnetic oxide of iron is 0.5 to 4 % of the weight on the basis of an iron element, and an iron element dissolving rate of this magnetic oxide of iron exists by 20 % of the weight. a ratio (B/A) with all the content A of a silicon element of this magnetic oxide of iron -- x100 being 44 to 84%, and, a ratio (C/A) of the content C of a silicon element and this content A which exist in the surface of this magnetic oxide of iron -- magnetic toner, wherein x100 is 10 to 55% and this binding resin is a mixture of a vinyl system polymer and polyester resin.

[Claim 2]In magnetic toner contained at least, binding resin and a magnetic oxide of iron this magnetic toner, In particle size distribution of this magnetic toner, a weight average particle size is 13.5 micrometers or less, and content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers is 50 or less % of the weight, and this magnetic oxide of iron, The content B of a silicon element in which content of a silicon element of this magnetic oxide of iron is 0.5 to 4 % of the weight on the basis of an iron element, and an iron element dissolving rate of this magnetic oxide of iron exists by 20 % of the weight. a ratio (B/A) with all the content A of a silicon element of this magnetic oxide of iron -- x100 being 44 to 84%, and, a ratio (C/A) of the content C of a silicon element and this content A which exist in the surface of this magnetic oxide of iron -- magnetic toner which x100 is 10 to 55%, and is characterized by the surface of a magnetic oxide of iron being processed by silicone oil or silicone varnish.

[Claim 3]Magnetic toner which contains binding resin and a magnetic oxide of iron at least, comprising:

In [a weight average particle size of this magnetic toner is 13.5 micrometers or less, and] particle size distribution of this magnetic toner, Content B of a silicon element in which content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers is 50 or less % of the weight, content of a silicon element of this magnetic oxide of iron of this magnetic oxide of iron is 0.5 to 4 % of the weight on the basis of an iron element, and an iron element dissolving rate of this magnetic oxide of iron exists by 20 % of the weight. a ratio (B/A) with all the content A of a silicon element of this magnetic oxide of iron -- x100 being 44 to 84%, and, a ratio (C/A) of the content C of a silicon element and this content A which exist in the surface of this magnetic oxide of iron -- x100 being 10 to 55%, and this binding resin, It is a copolymer obtained from a styrene system monomer and an acrylic system monomer at least, It has the acid value of 1-70 in THF insoluble matter and extractives, and molecular weight distribution of THF extractives has at least one peak in 2,000 or more molecular weights thru/or less than 15,000 in a GPC chart, and they are at least one peak or a shoulder to the molecular weights 15,000-100,000.

[Claim 4]The magnetic toner according to claim 3, wherein an acrylic system monomer in THF

insoluble matter is two or more sorts.

[Claim 5]The magnetic toner according to claim 3 or 4 which a weight average particle size of magnetic toner is 3.5–9 micrometers, and is characterized by content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers being 10 or less % of the weight in particle size distribution of this magnetic toner.

[Claim 6]In an image formation method which has the process of revolving speed of an outer diameter of an electrostatic charge image supporter which holds an electrostatic charge image on the surface being not less than 35 mm/sec, developing an electrostatic charge image on an electrostatic charge image supporter with a developer, and carrying out electrostatic image transfer of the developed image to a transfer material further, Magnetic toner in which this electrostatic charge image supporter and a transfer means are contacted with 10 or more g/cm of linear pressures, and this developer contains binding resin and a magnetic oxide of iron at least.

A non-subtlety granular material or hydrophobic inorganic matter pulverized coal.

Are the image formation method provided with the above, and content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers is 50 or less % of the weight, and this magnetic oxide of iron, The content B of a silicon element in which content of a silicon element of this magnetic oxide of iron is 0.5 to 4 % of the weight on the basis of an iron element, and an iron element dissolving rate of this magnetic oxide of iron exists by 20 % of the weight. a ratio (B/A) with all the content A of a silicon element of this magnetic oxide of iron -- a ratio (C/A) of the content C of a silicon element and this content A which $\times 100$ is 44 to 84%, and exist in the surface of this magnetic oxide of iron -- it is characterized by $\times 100$ being 10 to 55%.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to the magnetic toner and the image formation method for developing electro photography and the electrostatic charge latent image in the image formation method like electrostatic recording.

[0002]

[Description of the Prior Art] The method of developing using the magnetic toner which has conductivity electrically on U.S. Pat. No. 3,909,258 specifications is proposed. This supports conductive magnetic toner on the cylindrical conductive sleeve which has magnetism inside, makes this contact an electrostatic image and develops it. Under the present circumstances, in a developing section, a track is formed of particle toner between a record body surface and a sleeve surface, and an electric charge is led to particle toner from a sleeve through this track, and particle toner adheres to a picture part according to the Coulomb's force between the picture parts of an electrostatic image, and negatives are developed. Although the developing method using this conductive magnetic toner is an outstanding method which avoided the problem related to the conventional two-ingredient developing method, since an opposite side toner is conductivity, it has the problem that it is difficult to transfer the developed picture from a recording body electrostatically to final support members, such as a regular paper.

[0003] Developing methods using the magnetic toner of the high resistance which can be transferred electrostatically include the developing method using the charge polarization of particle toner. However, the method of starting has problems -- the concentration of the developed image with slow developing velocity is not fully obtained in essence -- and is difficult practically.

[0004] As other developing methods using the insulating magnetic toner of high resistance, frictional electrification of the particle toner is carried out by friction between particle toner, friction of particle toner, a sleeve, etc., etc., and the method of contacting an electrostatic image attachment component and developing this is known. However, the Coulomb's force between sleeves becomes strong and the particle toner charged [which becomes these methods have little contact frequency of particle toner and a friction member, and insufficient / methods / frictional electrification / easily] has a problem of being easy to condense on a sleeve. It was difficult practically.

[0005] However, in JP,55-18656,A etc., the new jumping developing method which removed the above-mentioned problem was proposed. This applies magnetic toner very thinly on a sleeve, carries out frictional electrification of this, subsequently to an electrostatic image, approaches extremely and develops this. Increase of the opportunity for a sleeve and a toner to contact when this method applies magnetic toner very thinly on a sleeve, and sufficient frictional electrification were made possible, The picture outstanding by making the condensation between particle toner fully rub against a sleeve with profit etc. is acquired by supporting magnetic toner by magnetism and moving a magnet and a toner relatively.

[0006] However, there are unstable factors in connection with the insulating toner to be used in

the developing method using the improved above-mentioned insulating toner. As for it, into the insulating toner, mixture dispersion of a considerable quantity of impalpable powder-like magnetic bodies is carried out.

Since these some magnetic bodies are exposed on the surface of particle toner, the kind of magnetic body influences the mobility of magnetic toner, and frictional electrification nature, and causes as a result change or degradation of the various characteristics required of magnetic toner, such as the developing characteristic of magnetic toner, and endurance.

[0007]In the jumping developing method using the magnetic toner which contains the conventional magnetic body if it says to details more, If the developing process (for example, copy) of a repetition of a long period of time is continued, the mobility of the developer containing magnetic toner gets worse, and normal frictional electrification is not acquired, but electrification becomes uneven easily, and in low-humidity/temperature environment, it will be easy to generate fogging development and will be easy to become a big problem on a toner image. When the adhesion of binding resin and the magnetic electrifying characteristic which constitute the magnetic toner particle is weak, there is a tendency to be able to take a magnetic body from the magnetic toner surface, and to have adverse effects, such as toner image density lowering, according to a repeated developing process.

[0008]When distribution of the magnetic body in the inside of a magnetic toner particle is uneven, the small magnetic toner particle of the particles contained mostly accumulates a magnetic body on a sleeve, and generating of the nonuniformity of the shade called an image concentration fall and a sleeve ghost may be seen.

[0009]Although the proposal about the magnetic oxide of iron contained in magnetic toner is proposed conventionally, it has a point which should still be improved.

[0010]For example, in JP,62-279352,A, the magnetic toner containing the magnetic oxide of iron containing a silicon element is proposed. Although this magnetic oxide of iron is making the silicon element exist in the inside of a magnetic oxide of iron intentionally, it has a point which should still be improved to the mobility of the magnetic toner containing this magnetic oxide of iron.

[0011]In JP,3-9045,B, it is adding a silicate and the proposal which controls the shape of a magnetic oxide of iron to a globular form is made. In order that the magnetic oxide of iron obtained by this method may use a silicate for control of particle shape, many silicon elements are distributed over the inside of a magnetic oxide of iron, The adhesion of binding resin and the magnetic oxide of iron which constitute magnetic toner becomes there is little abundance of the silicon element in the magnetic-oxide-of-iron surface, and a fluid improvement of magnetic toner and the smoothness of a magnetic oxide of iron are high, and insufficient easily.

[0012]In JP,61-34070,A, during the oxidation reaction to a tri-iron tetraoxide, a HIDOROSHISO silicate solution is added and the manufacturing method of the tri-iron tetraoxide is proposed. Although the tri-iron tetraoxide by this method has a Si element near the surface, near the tri-iron tetraoxide surface, a Si element accomplishes a layer, and exists, and it has the problem that the surface is weak to the mechanical shock like friction.

[0013]On the other hand, about fixing which is a final process for obtaining a print, the demand of low temperature fixation is increasing from a viewpoint of energy saving. The fixing method most general now is a sticking-by-pressure heating method with a heat roller.

[0014]The sticking-by-pressure heating method by a heating roller is established by making the surface of the heat roller which formed the surface with the material which has a mold-release characteristic to a toner pass through the toner image surface of a sheet to be established, contacting under application of pressure. It is very good, and the thermal efficiency at the time of welding a toner image on a sheet to be established can be established promptly, and this method has it in a high-speed electro photography copying machine in order to contact under application of pressure of the surface of a heat roller and the toner image of a sheet to be established. [dramatically effective] However, in a described method, in order that a heat roller surface and a toner image may contact under application of pressure by a molten state, a part of toner image adheres and transfers on the fixing roller surface, this re-transfers to the following

sheet to be established, what is called an offset phenomenon is produced, and a sheet to be established may be soiled. Keeping a toner from adhering to a heat fusing roller surface is set to one of the indispensable conditions of a heat roller fusing method.

[0015]The material which is the purpose which does not make a toner adhere to the fixing roller surface conventionally, and was excellent in the mold-release characteristic to the toner in the roller surface, for example, In order to form by silicone rubber, fluorine system resin, etc. and to prevent the prevention from offset, and fatigue of a roller surface on the surface further, covering a roller surface with the thin film of the good fluid of the mold-release characteristic like silicone oil is performed. However, this method has problems, like in that offset of a toner is prevented, although it is very effective, since the device for supplying the fluid for offset prevention is required, an anchorage device becomes complicated. So, the actual condition of the direction which prevents offset by supply of the fluid for offset prevention is that development of the high toner of the large offset-proof nature of a fixing temperature field is desired desirable rather. Then, since a mold-release characteristic is increased as a toner, the method of adding waxes which are enough fused at the time of heating, such as low molecular weight polyethylene and polypropylene, is also performed, but while it is effective in prevention from offset, the cohesiveness of a toner becomes unstable [increase and an electrifying characteristic], and tends to cause a durable fall. Then, the device which adds improvement to binder resin as other methods is tried [that it is various and].

[0016]For example, how to raise the glass transition temperature (Tg) and the molecular weight of binder resin in a toner, and raise the melt viscoelasticity of a toner is also known. However, when the offset phenomenon has been improved, such a method becomes insufficient [fixability] and the problem that the fixability under the degree of low temperature demanded in the formation of high-speed development or energy saving, i.e., low temperature fixability, is inferior produces it.

[0017]Generally, in order to improve the low temperature fixability of a toner, it is required that Tg and the molecular weight of the binder resin which needs to reduce the viscosity of the toner at the time of melting, and needs to enlarge adhesion area with a fixing substrate, for this reason is used should be made low.

[0018]If Tg of a binder is reduced, it will become easy to block a toner under an elevated temperature, and it will be concerned with preservation stability.

[0019]In order that heat sources, such as a fixing assembly and electric equipment, may approach a cleaner and a development counter dramatically with the miniaturization of a copying machine in recent years or a laser beam printer especially, reservation of the blocking resistance at 50 ** is needed at worst.

[0020]That is, it was dramatically difficult to satisfy simultaneously low temperature fixability, blocking resistance, and offset tightness.

[0021]Although the toner using the resin which polymerized the vinyl system monomer under existence of reactant polyester resin in JP,56-116043,A although this problem is solved, and it was made to polymers-ize via crosslinking reaction, an addition reaction, and a graft-ized reaction in process of a polymerization is proposed, The function of mutual resin cannot fully be efficiently employed in respect of low temperature fixability and offset tightness.

[0022]When it uses for one ingredient of magnetism developer, distribution of a magnetic oxide of iron becomes uneven easily.

[0023]Although the toner using the resin which blended two kinds (not less than 80% of a gelation degree and less than 10% of a gelation degree) of vinyl system resin in which polyester resin differs from a gel content simply is proposed by JP,1-15063,B, Although this thing is good about low temperature fixability, when it uses for an one-ingredient magnetic developer, distribution of a magnetic oxide of iron becomes uneven easily.

[0024]Thus, by the system which mixes polyester resin with a vinyl system polymer, and is used as binding resin, since the resin which has two kinds of different physical properties is used, as compared with the case where distribution of toner structure material, such as colorant to the inside of resin, uses resin of uniform composition, it is easy to become uneven. In the monocomponent toner especially used for jumping development, when distribution of a magnetic

body becomes uneven, there is a tendency for the dot reproducibility aggravation by spilling generating of fogging or a toner to be conspicuous, in the image output test over thousands of more sheets, density lowering is conspicuous, and it is not desirable practically. That is, when mixing polyester resin with a vinyl system polymer and using for one-ingredient magnetic toner, satisfying fixability, offset nature, and imaging quality simultaneously is not yet attained.

[0025]Although the function of the image forming device using the electrophotographic technology like a copying machine and a laser beam printer is diversified and highly-minutiae-izing of a toner image and high definition-ization are called for further in recent years, In order to reappear faithfully, without being crushed or disrupted until it results in a very detailed latent image, it is effective to diameter[of a granule]-ize particle toner as proposed by JP,1-112253,A. However, it is easy to produce a fall and above various evils of the efficiency of comminution by generating of weld of the toner composition to the grinder wall in a grinding process, etc., so that it is going to make the particle diameter of a toner small.

[0026]Since it falls, the mobility of a toner can so raise mobility easily that toner particle diameter becomes small, if a lot of non-subtlety granular materials for fluid maintenance of a toner are added, but. It becomes the cause of damaging a photo conductor, and becomes easy to generate weld of the toner to a photo conductor, filming, etc., and toner scattering etc. get worse.

[0027]Otherwise, although a lot of image formation methods which can be copied or printed out are wished for a short time with rationalization of rapid clerical work in recent years, In the comparatively quick image formation method of the revolving speed of the outer diameter of a latent-image-keeping object, there is also a problem which the inferior transfer called the "transfer middle omission" from which the picture outputted turns into a picture of only a contour part tends to produce.

[0028]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the magnetic toner which solved the problem like ****.

[0029]The purpose of this invention has high image concentration, and there is in providing image reproducibility outstanding magnetic toner.

[0030]The purpose of this invention is to provide the magnetic toner which there is no fogging also in prolonged use and has stable electrification performances.

[0031]The purpose of this invention is to provide the good magnetic toner of fixability and offset-proof nature.

[0032]The purpose of this invention is to provide magnetic toner with high image concentration also in the durability over the long period of time under a high-humidity environment.

[0033]The purpose of this invention is established at a low temperature, and is excellent in offset-proof nature and blocking resistance, and there is in providing the magnetic toner which does not have an adverse effect on performance in the high temperature atmosphere in a small aircraft in particular.

[0034]The purpose of this invention is to provide efficient producible magnetic toner, without excelling in the grindability in the grinding process at the time of toner production, and generating weld with a device wall.

[0035]In the image formation method by application-of-pressure transfer like the contact transfer method, the purpose of this invention is not based on the conditions of a transfer material, but there is in providing the image formation method which has a transfer process from which a high-definition picture faithful to a latent image is acquired.

[0036]The purpose of this invention is to provide the image formation method with which there are no phenomena, such as "extract during transfer", or this phenomenon is controlled.

[0037]Even if various transfer materials, such as a thick transfer paper, are used for the purpose of this invention, there is in providing the image formation method which uses the toner which gives a quality picture without a transfer middle omission.

[0038]

[Means for Solving the Problem and its Function]In magnetic toner contained at least, this invention binding resin and a magnetic oxide of iron this magnetic toner, In particle size

distribution of this magnetic toner, a weight average particle size is 13.5 micrometers or less, and content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers is 50 or less % of the weight, and this magnetic oxide of iron, The content B of a silicon element in which content of a silicon element of this magnetic oxide of iron is 0.5 to 4 % of the weight on the basis of an iron element, and an iron element dissolving rate of this magnetic oxide of iron exists by 20 % of the weight. a ratio (B/A) with all the content A of a silicon element of this magnetic oxide of iron -- x100 being 44 to 84%, and, a ratio (C/A) of the content C of a silicon element and this content A which exist in this magnetic-oxide-of-iron surface -- x100 is 10 to 55%, and this binding resin is related with magnetic toner being a mixture of a vinyl system polymer and polyester resin. Below, "this invention 1" means this magnetic toner.

[0039]This invention binding resin and a magnetic oxide of iron in magnetic toner contained at least this magnetic toner, In particle size distribution of this magnetic toner, a weight average particle size is 13.5 micrometers or less, and content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers is 50 or less % of the weight, and this magnetic oxide of iron, The content B of a silicon element in which content of a silicon element of this magnetic oxide of iron is 0.5 to 4 % of the weight on the basis of an iron element, and an iron element dissolving rate of this magnetic oxide of iron exists by 20 % of the weight. a ratio (B/A) with all the content A of a silicon element of this magnetic oxide of iron -- x100 being 44 to 84%, and, a ratio (C/A) of the content C of a silicon element and this content A which exist in the surface of this magnetic oxide of iron -- x100 is 10 to 55%, and it is related with magnetic toner, wherein the surface of a magnetic oxide of iron is processed by silicone oil or silicone varnish. Below, "this invention 2" means this magnetic toner.

[0040]This invention binding resin and a magnetic oxide of iron in magnetic toner contained at least this magnetic toner, In particle size distribution of this magnetic toner, a weight average particle size is 13.5 micrometers or less, and content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers is 50 or less % of the weight, and this magnetic oxide of iron, The content B of a silicon element in which content of a silicon element of this magnetic oxide of iron is 0.5 to 4 % of the weight on the basis of an iron element, and an iron element dissolving rate of this magnetic oxide of iron exists by 20 % of the weight. a ratio (B/A) with all the content A of a silicon element of this magnetic oxide of iron -- x100 being 44 to 84%, and, a ratio (C/A) of the content C of a silicon element and this content A which exist in the surface of this magnetic oxide of iron -- x100 being 10 to 55%, and this binding resin, It is a copolymer obtained from a styrene system monomer and an acrylic system monomer at least, Have the acid value of 1-70 in THF insoluble matter and extractives, and molecular weight distribution of THF extractives has at least one peak in 2,000 or more molecular weights thru/or less than 15,000 in a GPC chart, Are resin which has at least one peak or a shoulder in the molecular weights 15,000-100,000, and Tg of this toner 45-65 **, THF insoluble matter is related with magnetic toner characterized by being 20 or more weight sections to resinous principle 100 weight section. Below, "this invention 3" means this magnetic toner.

[0041]Revolving speed of an outer diameter of an electrostatic charge image supporter to which this invention holds an electrostatic charge image on the surface is not less than 35 mm/sec, In an image formation method which has a process which develops an electrostatic charge image on an electrostatic charge image supporter with a developer which has a toner, and carries out electrostatic image transfer to a transfer material further, This electrostatic charge image supporter and a transfer means are contacted with 10 or more g/cm of linear pressures, and this developer, Are magnetic toner which contains binding resin and a magnetic oxide of iron at least, and a non-subtlety granular material or hydrophobic inorganic matter pulverized coal a magnetic developer which it has, and this magnetic toner, In particle size distribution of this magnetic toner, a weight mean diameter is 13.5 micrometers or less, and content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers is 50 or less % of the weight, and this magnetic oxide of iron, The content B of a silicon element in which content of a silicon element of this magnetic oxide of iron is 0.5 to 4 % of the weight on the basis of an iron element, and an iron element dissolving rate of this magnetic oxide of iron exists by 20 % of the weight. a ratio (B/A) with all the content A of a silicon element of this magnetic oxide of iron -- a ratio

(C/A) of the content C of a silicon element and this content A which $\times 100$ is 44 to 84%, and exist in the surface of this magnetic oxide of iron -- $\times 100$ is related with an image formation method characterized by what is been 10 to 55%. Below, "this invention 4" means this image formation method.

[0042]In magnetic toner of this invention, although a reason which the desired end can attain is not necessarily clear, it is presumed as follows.

[0043]Namely, in [in magnetic toner of this invention, a weight average particle size is 13.5 micrometers or less (preferably 3.5–13.5 micrometers), and] particle size distribution of magnetic toner, It is one of the features that content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers uses a specific magnetic oxide of iron containing a silicon element for magnetic toner which is 50 or less % of the weight.

[0044]When a weight average particle size of magnetic toner exceeds 13.5 micrometers, Or in magnetic toner containing many comparatively coarse magnetic toner particles, when content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers exceeds 50 % of the weight, even if it uses a magnetic oxide of iron generally used from before, electrification stabilization of magnetic toner is possible.

[0045]Since the mobility of magnetic toner becomes low even if it uses a special magnetic oxide of iron of this invention and it becomes easy to generate problems, such as fogging by poor electrification, and dark degree ****, when a weight average particle size of a magnetic toner particle is smaller than 3.5 micrometers, not less than 3.5 micrometers of a weight average particle size are preferred.

[0046]That that is, a prominent effect is seen in magnetic toner of this invention as compared with conventional examples, such as an electrifying stability and fluid improvement, It is a case where a weight average particle size is 13.5 micrometers or less (preferably 3.5–13.5 micrometers, more preferably 5.0–13.0 micrometers), and content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers is 50 or less (preferably 40% or less) % of the weight.

[0047]It is one of the features that content of a silicon element of a magnetic oxide of iron furthermore used for magnetic toner by this invention is 0.5 to 4.0 % of the weight (preferably 0.8 to 3.0 % of the weight, still more preferably 0.9 to 3.0 % of the weight) on the basis of an iron element. When there is less content of a silicon element than 0.5 % of the weight, An improvement effect (improvement of the mobility of especially magnetic toner) of magnetic TONAHE is weak, and when there is more content of a silicon element than 4.0 % of the weight, a silicic acid ingredient remains on the magnetic-oxide-of-iron surface more than needed, or tends to have an adverse effect on magnetic properties, and is not preferred.

[0048]All the content A of a silicon element which furthermore exists in a magnetic oxide of iron used for magnetic toner by this invention. Ratio B/A $\times 100$ (%) with the content B of a silicon element in which an iron element dissolving rate of this magnetic oxide of iron exists by about 20% is 44 to 84% (preferably 60 to 80%), It is one of the features that ratio C/A $\times 100$ (%) of content [of a silicon element] C and content A which exist in particle surface of this magnetic oxide of iron 100 (%) is 10 to 55% (preferably 25 to 40%). B/A $\times 100$ (%) may exist in a center section of a magnetic oxide of iron so much [when smaller than 44% / a silicon element more than needed], and, in addition to manufacturing efficiency getting worse easily, magnetic properties may serve as an unstable magnetic oxide of iron.

[0049]When B/A $\times 100$ (%) exceeds 84%, many silicon elements exist in a layer part of a magnetic oxide of iron too much, a silicon element exists in the magnetic-oxide-of-iron surface so much in layers, the magnetic-oxide-of-iron surface becomes weak to a mechanical shock, and when it uses for magnetic toner, it is easy to generate many evils.

[0050]On the other hand, C/A $\times 100$ (%) in being smaller than 10%, In addition to there being few silicon elements on the surface of a magnetic oxide of iron, and good mobility not being easily obtained by a magnetic oxide of iron and magnetic toner, electrification quantity and a volume specific resistance value of a magnetic oxide of iron fall, and it is easy to spoil the electrifying stability of magnetic toner, and environmental stability.

[0051]If C/A $\times 100$ (%) increases more than 55%, when unevenness on the surface of a magnetic

oxide of iron will be conspicuous and magnetic toner will be manufactured, an uneven portion on the surface of a magnetic oxide of iron serves as a piece of **, and it distributes in magnetic toner, and it is easy to have an adverse effect on the magnetic toner characteristic.

[0052]That is, in order to obtain the characteristic of good magnetic toner, it is preferred that distribution of a silicon element which exists in a magnetic oxide of iron increases continuously or gradually, and goes toward the surface from an inside as described above.

[0053]Furthermore in this invention, electrification quantity of a magnetic oxide of iron is -25 -- 70microc/g (preferably -40 -- 60microc/g), And it is preferred that volume specific resistance values of a magnetic oxide of iron are 1×10^4 -- 1×10^8 omega-cm (preferably 5×10^4 -- 5×10^7 omega-cm).

[0054]If long term use of the magnetic toner is repeated and carried out when electrification quantity of a magnetic oxide of iron is less than -25microc/g, it will become impossible to be easy to have the electrification quantity which magnetic toner needs, and problems, such as a fall of image concentration and image fogging, will occur. On the other hand, when electrification quantity of a magnetic oxide of iron exceeds -70microc/g, electrification quantity of magnetic toner becomes high too much, and a fall of image concentration is easy to see in low temperature and damp environment.

[0055]When a volume specific resistance value of a magnetic oxide of iron is smaller than 5×10^3 omega-cm, it becomes difficult easily to hold electrification quantity which magnetic toner needs, and a fall of image concentration takes place easily. On the other hand, when a volume specific resistance value of a magnetic oxide of iron exceeds 1×10^8 omega-cm, on the occasion of repeated use in low temperature and damp environment, electrification quantity becomes high more than needed easily, and a fall of image concentration is easy to see.

[0056]It is preferred that the degree of condensation of a magnetic oxide of iron is furthermore 3 to 40% (preferably 5 to 30%) in this invention.

[0057]When the degree of condensation of a magnetic oxide of iron is smaller than 3%, it is difficult to be easy to generate blow off of magnetic toner called flashing at the time of magnetic toner manufacture, and to manufacture magnetic toner efficiently.

[0058]On the other hand, when the degree of condensation exceeds 40%, fully distributing a magnetic oxide of iron to inside of magnetic toner tends to have an adverse effect on image concentration, fogging, etc. rather than it is easy. When the mobility of a magnetic oxide of iron is reflected in the mobility of magnetic toner and the degree of condensation uses a magnetic oxide of iron exceeding 40% in this invention, The mobility of magnetic toner is fully hard to be obtained, and it has an adverse effect on the electrostatic property of magnetic toner, and is in a tendency for generating of inferior transfers, such as a "middle omission", besides generating of fogging etc. to be seen.

[0059]It is preferred that the smoothness D of a magnetic oxide of iron is 0.2--0.6 (preferably 0.3--0.5) in this invention.

[0060]If the smoothness D is smaller than 0.2, unevenness on the surface of a magnetic oxide of iron will be conspicuous, an uneven portion will serve as a piece of ** at the time of magnetic toner manufacture, and it will distribute in magnetic toner, and will be easy to have an adverse effect on a toner characteristic.

[0061]On the other hand, sufficient adhesion of binding resin and a magnetic oxide of iron by which the smoothness D is used for magnetic toner when larger than 0.6 is hard to be acquired, a magnetic oxide of iron on the surface of magnetic toner can be gradually taken in repeated use, and it is easy to have adverse effects, such as an image concentration fall.

[0062]It is preferred that the degree of sphericity psi of a magnetic oxide of iron is 0.8 or more in this invention.

[0063]In being smaller than 0.8, each particle of a magnetic oxide of iron serves as a form where it contacts in a field and a field, and the degree of sphericity psi in small magnetic-oxide-of-iron particles near particle diameter of 0.1--1.0 micrometer. Even if it carries out with mechanical shearing force, a magnetic-oxide-of-iron particle comrade cannot be pulled apart easily, therefore a magnetic oxide of iron of HE in magnetic toner may fully be unable to be distributed.

[0064]As for a magnetic oxide of iron used for this invention, it is preferred that mean particle diameter has preferably 0.1–0.3 micrometer 0.1–0.4-micrometer.

[0065]It is one of the features to carry out hydrophobing processing of the surface of a magnetic oxide of iron used for magnetic toner with silicone oil or a silicone varnish by this invention 2 furthermore. By carrying out hydrophobing processing of this magnetic oxide of iron that has silica near the surface, the moisture absorption-proof characteristic improves and image concentration under highly humid is stabilized more.

[0066]As for a throughput of silicone oil or a silicone varnish, it is preferred that it is 0.05 to 5 % of the weight (preferably 0.08 to 3 % of the weight) to 100 % of the weight of magnetic oxides of iron. When sufficient hydrophobing processing cannot be performed when there are few throughputs than 0.05 % of the weight, but a throughput exceeds 5 % of the weight, a magnetic oxide of iron condenses and it becomes a use top problem.

[0067]A measuring method of various-physical-properties data in this invention is explained in full detail below.

(1) Although particle size distribution of a particle-size-distribution toner of a toner can be measured by various methods, carry out using a Coulter counter in this invention.

[0068]Namely, as a measuring device, a Coulter counter TA-II type (made by a coal tar company) is used, Connecting an interface (product made from the department machine of a day) and CX-1 personal computer (made by Canon) which output number distribution and volume distribution, an electrolysis solution prepares a NaCl aqueous solution 1% using the 1st class sodium chloride. As a measuring method, 0.1–5 ml of surface-active agents (preferably alkylbenzene sulfonates) are added as a dispersing agent into said 100–150 ml of electrolytic water solutions, and 2–20 mg of test portions are added further. An electrolysis solution suspended in a sample performs distributed processing for about 1 to 3 minutes with an ultrasonic dispersion machine, and it computes volume distribution and number distribution of a 2–40-micrometer particle by measuring volume of a toner, and the number with said Coulter counter TAII type, using a 100-micrometer aperture as an aperture. And it asks for the not less than 12.7-micrometer gravimetric analysis of a weight reference searched for from weight mean diameter D_4 (let the median of each channel be a central value for every channel) of a weight reference searched for from volume distribution concerning this invention, and volume distribution.

(2) In content this invention of a silicon element, the content C of a silicon element on the surface of a magnetic oxide of iron can be calculated by following methods. For example, it warms with a water bath so that about 3 l. of deionized water may be put into a 5-l. beaker and it may become 50–60 **. It adds into a 5-l. beaker with this deionized water, rinsing about 25 g of magnetic oxides of iron made into a slurry by about 400 ml of deionized water by about 300 ml of deionized water.

[0069]Subsequently, keeping temperature at about 60 ** and keeping churning speed at about 200 rpm, best sodium hydroxide shall be added and magnetic-oxide-of-iron concentration shall be about 5 g/l as about 1-N sodium hydroxide solution at this time. The dissolution of a silicon compound like silicic acid of a magnetic-oxide-of-iron particle surface is started. 20 ml is sampled 30 minutes after a dissolution start, it filters with a 0.1micro membrane filter, and a filtrate is extracted. Plasma emission spectroscopy (ICP) performs a fixed quantity of a silicon element for a filtrate.

[0070]The content C of a silicon element is equivalent to silicon element concentration (mg/l) of per a unit weight (5 g/l of magnetic oxides of iron) of a magnetic oxide of iron in sodium hydroxide solution.

[0071]In this invention, content (based on an iron element) of a silicon element of a magnetic oxide of iron, a dissolution rate of an iron element, and the content A and B of a silicon element can be calculated by following methods. For example, it warms with a water bath so that about 3 l. of deionized water may be put into a 5-l. beaker and it may become 45–50 **. It adds into a 5-l. beaker with this deionized water, rinsing about 25 g of magnetic oxides of iron made into a slurry by about 400 ml of deionized water by about 300 ml of deionized water.

[0072] Subsequently, keeping temperature at about 50 ** and keeping churning speed at about 200 rpm, best chloride is added and the dissolution is started. At this time, magnetic-oxide-of-iron concentration will be about 5 g/l, and a hydrochloric acid aqueous solution has become about 3 N. From a dissolution start, by the time it dissolves altogether and becomes transparent, about 20 ml will be sampled several times, and it filters with a 0.1 micro membrane filter, and a filtrate is extracted. Plasma emission spectroscopy (ICP) performs a fixed quantity of an iron element and a silicon element for a filtrate.

[0073] By a following formula, an iron element dissolving rate for every sample is calculated.

[0074]

[Equation 1]

$$\text{鉄元素溶解率\%} = \frac{\text{サンプル中の鉄元素濃度 (mg/l)}}{\text{完全に溶解した時の鉄元素濃度 (mg/l)}} \times 100$$

The content and content of a silicon element for every sample are calculated by a following formula.

[0075]

[Equation 2]

$$\text{ケイ素元素の含有率 (\%)} = \frac{\text{ケイ素元素濃度 (mg/l)}}{\text{鉄元素濃度 (mg/l)}} \times 100$$

All the content A of the silicon element of a magnetic oxide of iron is equivalent to the silicon element concentration (mg/l) of per the unit weight (5 g/l of magnetic oxides of iron) of the magnetic oxide of iron after dissolving altogether.

[0076] The content B of a silicon element of a magnetic oxide of iron is equivalent to silicon element concentration (mg/l) of per a unit weight (5 g/l of magnetic oxides of iron) of a magnetic oxide of iron detected, when a dissolution rate of a magnetic oxide of iron is 20%.

[0077] As a method of measuring the content A, B, and C, ** While measuring content and the content A and B of a silicon element by dividing into two, a sample of a magnetic oxide of iron. The content C of a method of measuring the content C separately and a sample of ** magnetic oxide of iron is measured. It ranks second using a sample after measurement, content B' (quantity which subtracted the content C from the content B), and content A' (quantity which subtracted the content C from the content A) are measured, and a method of computing the content A and B eventually, etc. are mentioned.

(3) About 2 g of electrification quantity magnetic oxides of iron and about 198 g of career iron powder (TEFV200 – 300mesh) of a magnetic oxide of iron (Japanese Iron powder) are *****(ed) into a 500-ml poly bottle. After shaking for 10 seconds by hand, it shakes for 20 minutes by V type BUNRENDA, and electrification quantity of a magnetic oxide of iron is measured using a blowing off granular material electrification quantity measuring device (Toshiba Chemical CORP.). At this time, stainless steel net producing of 400mesh is set to a FARA day gauge for measurement, 0.4 g of measurement ***** are *****(ed), and it computes from a value when blowing off is performed for 30 seconds.

(4) Put 10 g of volume specific resistance value magnetic oxides of iron of a magnetic oxide of iron into a measuring cell, and mold with an oil hydraulic cylinder (** 600 kg/cm²). After releasing a pressure, a ohm-meter (product YEW MODEL made from YOKOGAWA electrical and electric equipment 2506 A DIGITAL MALTIMETOR) is set, and a pressure of 150 kg/cm² is again applied with an oil hydraulic cylinder. Measurement is started and measured value of 3 minutes after is read. Furthermore thickness of the amount of trials is measured and a volume specific resistance value is measured from a lower type.

[0078]

[Equation 3]

$$\text{体積固有抵抗値 (\Omega \cdot cm)} = \frac{\text{測定抵抗値 (\Omega) } \times \text{試料断面積 (cm}^2\text{)}}{\text{試料厚さ (cm)}}$$

(5) A mixer grinds 10 g of condensation degree magnetic oxides of iron of a magnetic oxide of iron, and **** the thing which made the sieve of 200mesh pass 2g. From a top, in order of 60mesh, 100mesh, and 200mesh, put three steps of sieves on a powder tester (Hosokawa Micron), and they are set to him, 2 g of samples which ****(ed) are calmly put on a sieve, the weight of the magnetic oxide of iron which gave vibration with an amplitude of 1 mm for 65 seconds, and remained on each sieve is measured, and the degree of condensation is computed according to a lower type.

[0079]

[Equation 4]

$$\text{凝聚度} = \frac{(60\text{ mesh 残試料の重量})}{(フルイに乗せた試料の重さ)} \times 100$$

$$+ \frac{(100\text{ mesh 残試料の重量} \times \frac{3}{5})}{(フルイに乗せた試料の重さ)} \times 100$$

$$+ \frac{(200\text{ mesh 残試料の重量} \times \frac{1}{5})}{(フルイに乗せた試料の重さ)} \times 100$$

(6) Ask for the smoothness D of a magnetic oxide of iron as follows in smoothness this invention of a magnetic oxide of iron.

[0080]

[Equation 5]

$$\text{平滑度 D} = \frac{\text{平均粒径より算出した磁性酸化鉄の表面積 (m}^2/\text{g})}{\text{実測して得た磁性酸化鉄の BET (m}^2/\text{g})}$$

(7) Yuasa Ionics make and amount measuring device of full automatic gas adsorption:auto SOBU 1 is used for the BETBET specific surface area of a magnetic oxide of iron, it uses nitrogen for adsorption gas, and asks for it by a BET multipoint method. As pretreatment of a sample, deaeration of 1 hour is performed at 50 **.

(8) Using the sample of the magnetic oxide of iron processed to the collodion membrane copper mesh with mean particle diameter and the surface area electron microscope (Hitachi H-700H) of the magnetic oxide of iron, with the applied voltage of 100 kV, take a photograph by 10,000 times and make it one 30,000 times the last magnification of this as one 3 times the baking magnification of this. By this, shape is observed, the maximum length (micrometer) of each particle is measured, 100 pieces are selected at random, and it is considered as mean particle diameter with the average.

[0081]For calculation of surface area, it assumes that it is the globular form which made a diameter mean particle diameter of a magnetic oxide of iron, density of a magnetic oxide of iron is measured by a usual method, and a value of surface area is calculated.

(9) Perform calculation of the degree of sphericity psi of a magnetic oxide of iron in degree-of-sphericity this invention of a magnetic oxide of iron as follows.

[0082]

[Equation 6]

$$\text{球形度 } \phi = \frac{\text{酸化磁性体の最小長 } (\mu\text{ m})}{\text{酸化磁性体的最大長 } (\mu\text{ m})}$$

The degree of sphericity psi should select 100 magnetic-oxide-of-iron particle samples out of the photograph at random, should measure maximum length and minimum length, and,

subsequently should average the calculated value.

[0083]The maximum length of an oxidation magnetic body and minimum length follow the method of asking for mean particle diameter.

[0084]As for 0.8 or more (0.9 or more [0.85 or more / Preferably / more preferably]) magnetic oxides of iron, the degree of sphericity psi preferably used for this invention has the shape of approximation in a spherical shape without an angular end to the degree of sphericity psi of the cubic usual magnetic oxide of iron being less than [of about 0.6-0.7] 0.8.

[0085]Since it is inferior to the case where the dispersibility to binding resin is 0.8 or more though the silicon element is unevenly distributed in the magnetic-oxide-of-iron particle surface when the degree of sphericity psi is less than 0.8, the developing characteristic of the magnetic toner obtained falls easily, and there is a tendency which becomes dot reproducibility inferior magnetic toner easily.

[0086]As for a magnetic oxide of iron used for magnetic toner of this invention, it is preferred to use 20 weight sections thru/or 200 weight sections to binding resin 100 weight section. It is good to use 30 to 150 weight section still more preferably.

[0087]A magnetic oxide of iron used for magnetic toner of this invention may be processed by silane coupling agent, a titanium coupling agent, titanate, an aminosilane, etc. by a case.

[0088]As for a magnetic oxide of iron used for this invention 2, it is indispensable to be processed with silicone oil or a silicone varnish, and as desirable silicone oil, A thing of about 30 to 1,000 centistokes is used for viscosity at 25 **, For example, dimethyl silicone oil, methyl hydrogen silicone oil, methylphenyl silicone oil, alpha-methylstyrene modified silicone oil, KURORU phenyl silicone oil, fluoride modified silicone oil, etc. are preferred.

[0089]A method of silicone oil processing is good also by a method of injecting silicone oil to silica which may mix a magnetic oxide of iron and silicone oil directly using mixers, such as a Henschel mixer, and serves as a base. Or after making a suitable solvent dissolve or distribute silicone oil, a magnetic oxide of iron of a base may be mixed, and a solvent may be removed and produced.

[0090]The silicone varnish used for this invention 2 can use a publicly known substance. For example, although Shin-etsu silicone company make, KR-251, and KP-112 grade are mentioned, it is not limited to this.

[0091]As the method of silicone varnish treated, the same known art as oil processing can be used.

[0092]As binding resin of a toner concerning this inventions 2 and 4, Styrene, such as polystyrene and polyvinyl toluene, and a single polymer of the substitution product; A styrene propylene copolymer, A styrene vinyltoluene copolymer, a styrene vinylnaphthalene copolymer, A styrene methyl acrylate copolymer, a styrene ethyl acrylate copolymer, A styrene butyl acrylate copolymer, a styrene acrylic acid octyl copolymer, A styrene acrylic acid dimethylaminoethyl copolymer, a styrene methacrylate [methyl] copolymer, A styrene methacrylate [ethyl] copolymer, a styrene methacrylate [butyl] copolymer, A styrene dimethylaminoethyl methacrylate copolymer, a styrene vinylmethyl ether copolymer, A styrene vinylethyl ether copolymer, a styrene vinyl methyl ketone copolymer, A styrene butadiene copolymer, a styrene isoprene copolymer, a styrene maleic acid copolymer, Styrene system copolymers, such as a styrene ester maleate copolymer; Polymethylmethacrylate, polybutyl methacrylate, polyvinyl acetate, polyethylene, polypropylene, a polyvinyl butyral, silicon resin, They can use it, polyester resin, polyamide resin, an epoxy resin, polyacrylic resin, rosin, denaturation rosin, ten pel resin, phenol resin, aliphatic series or alicycle fellows hydrocarbon resin, aromatic system petroleum resin, paraffin wax, carnauba wax, etc. being able to be independent, or mixing them. In particular, a styrene system copolymer and polyester resin are preferred in respect of a developing characteristic, fixability, etc.

[0093]A hydrocarbon system wax and an ethylene system olefin polymer may be used for a toner of this invention with binding resin as a fixing adjuvant.

[0094]In what is applied here as an ethylene system olefin single polymer or an ethylene system olefine copolymer. Polyethylene, polypropylene, ethylene propylene rubber, an ethylene-vinylacetate copolymer, What there are an ionomer etc. which have an ethylene-ethyl acrylate

copolymer and a polyethylene skeleton, and contains more than 50 mol % (preferably 60-mol % more than) for an olefin monomer in the above-mentioned copolymer is preferred.

[0095]On the other hand, this inventions 1 and 3 have the feature also in binding resin.

[0096]Binding resin concerning this invention 1 is a mixture of a vinyl system polymer and polyester resin.

[0097]A glass transition point (Tg) of a vinyl system copolymer is 45–65 ** (preferably 50–65 **), In molecular weight distribution of tetrahydrofuran (THF) extractives, it is desirable a field of the molecular weights 5,000–3,000,000 of a gel-permeation-chromatography (GPC) chart and to have a peak or a shoulder in 10,000–2,000,000 more preferably.

[0098]A glass transition point (Tg) polyester resin 50–70 **, desirable -- 55–65 ** and number average molecular weight Mn -- 1,500–10,000 -- 4,000–300,000, and that it is 6,000–200,000 preferably have 2,000–8,500, and the preferably desirable weight average molecular weight Mw. As for the mixture ratio of a vinyl system polymer and polyester resin, it is desirable that it is 9:1–2:8.

[0099]Here, a peak of chromatogram by GPC of THF extractives or/and a molecular weight of a shoulder are measured on the following conditions.

[0100]That is, a column is stabilized in a 40 ** heat chamber, in a column at this temperature, THF is passed at the rate of flow of 1 ml/m as a solvent, and about 100microl pouring of the THF sample solution is carried out, and it is measured. In the determination of molecular weight of a sample, molecular weight distribution which a sample has was computed from a relation of an opposite numerical value of an analytical curve and a count number which were produced by several sorts of monodisperse polystyrene standard samples. As a standard polystyrene sample for analytical curve creation, for example A product made from Pressure Chemical Co. Or it is appropriate that Oriental soda industrial company make and a molecular weight by Showa Denko K.K. use a standard polystyrene sample of about at least ten points using what is 10^2 – 10^8 grade. RI (refractive index) detector is used for a detector.

[0101]In order to measure a molecular weight region of 10^2 – 3×10^7 as a column, Combination of shodex GPC KF-801 by Showa Denko K.K. with sufficient combining two or more commercial polystyrene gel columns, and 802, 803 and 804,805,806,800p, Combination of URUTO raster Choerodon azurio gell 500 A-THF made from Water, 10^3 A-THF, 10^4 A-THF, 10^5 A-THF, and 10^6 A-THF or combination of A-Toluene series can be mentioned.

[0102]In order to measure a molecular weight region of 10^2 – 2×10^8 , combination of shodex GPCKF-801, and 802, 803 and 804,805,806,800p can be mentioned.

[0103]The following is raised as comonomer for obtaining a vinyl system copolymer which is a part of constituent of binding resin of this invention 1.

[0104]For example, styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-methoxy styrene, p-phenylstyrene, p-KURORU styrene, 3,4-dichloro styrene, p-ethylstyrene, 2,4-dimethylstyrene, p-n-butylstyrene, p-tert-butylstyrene, p-n-hexylstyrene, p-n-octylstyrene, p-n-nonylstyrene, p-n-decylstyrene, Styrene and its derivatives, such as p-n-dodecylstyrene; Ethylene, Unsaturation polyenes, such as ethylene unsaturation monoolefins; butadiene, such as propylene, butylene, and isobutylene; VCM/PVC, Vinylic halide, such as a vinylidene chloride, vinyl bromide, and **-ized vinyl; Vinyl acetate, Vinyl ester, such as vinyl propionate and BENZOE acid vinyl; Methyl methacrylate, Ethyl methacrylate, methacrylic acid propyl, n-butyl methacrylate, Methacrylic acid isobutyl, n-octyl methacrylate, methacrylic acid dodecyl, methacrylic acid-2-ethylhexyl, stearyl methacrylate, methacrylic acid phenyl, dimethylaminoethyl methacrylate, alpha-methylene aliphatic-monocarboxylic-acid ester species, such as diethylaminoethyl methacrylate; Methyl acrylate, Ethyl acrylate, acrylic acid n-butyl, isobutyl acrylate, Acrylic acid propyl, acrylic acid n-octyl, acrylic acid dodecyl, 2-ethylhexyl acrylate, acrylic acid stearyl, acrylic acid 2-KURORU ethyl, Acrylic ester, such as acrylic acid phenyl; Vinylmethyl ether, Vinyl ether, such as vinyl ethyl ether and vinyl isobutyl ether; Vinyl methyl ketone, Vinyl ketone; N-vinylpyrrole, such as vinyl hexyl ketone and methyl isopropenyl ketone, N-vinyl compound; vinylnaphthalene, such as N-vinylcarbazole, N-vinylindole, and N-vinyl

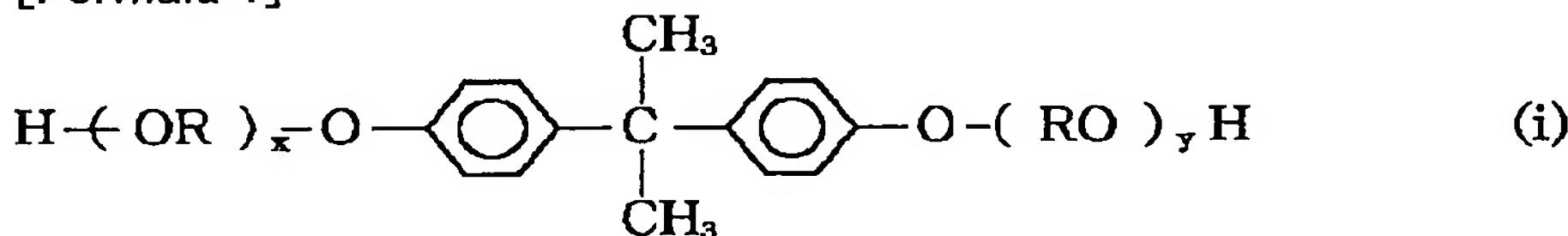
pyrrolidone; Acrylonitrile, Acrylic acid or methacrylic acid derivatives, such as a methacrylonitrile and acrylamide; a vinyl system monomer is independent or is used or more by two.

[0105]The presentation of polyester resin used by this invention 1 is as follows.

[0106]As a divalent alcohol component, ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, A diethylene glycol, triethylene glycol, 1,5-pantanediol, 1,6-hexanediol, neopentyl glycol, 2-ethyl-1,3-hexandiol, hydrogenation bisphenol A, a bisphenol expressed with a (i) type, and its derivative;

[0107]

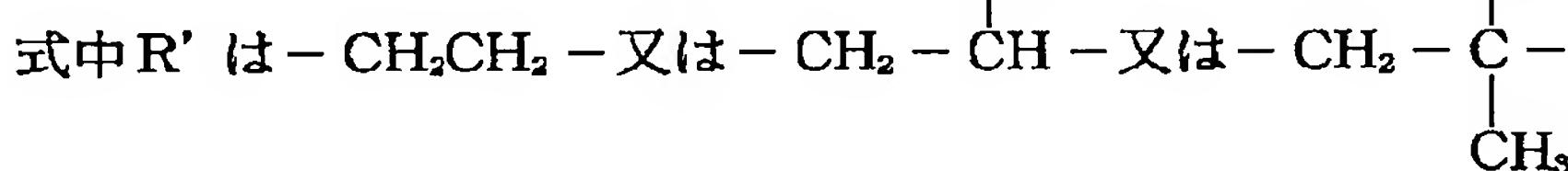
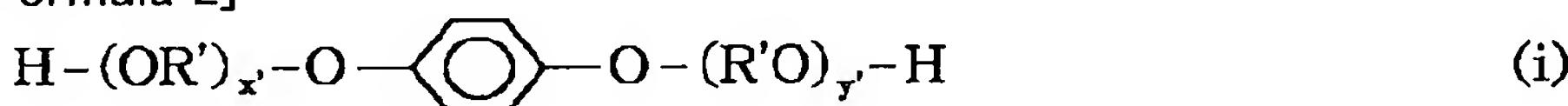
[Formula 1]



(It is ethylene or a propylene group, and x and y are zero or more integers, respectively, and the average value of x+y of the inside R of a formula is 0~10.) Diol shown by a (ii) formula again;

[0108]

[Formula 2]



x', y' は、0以上の整数であり、かつ、 $x + y$ の平均値は 0~10 である。

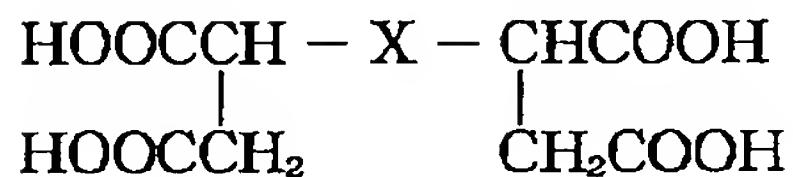
[0109]As a divalent acid component, benzenedicarboxylic acid or anhydrides of those, such as phthalic acid, terephthalic acid, isophthalic acid, and phthalic anhydride, Lower alkyl ester; Alkyl dicarboxylic acid or anhydrides of those, such as succinic acid, adipic acid, sebacic acid, and azelaic acid, Lower alkyl ester; Alkenyl succinic acid or alkyl succinic acid, such as n-dodecetyl succinic acid and n-dodecylsuccinic acid, Dicarboxylic acid, such as unsaturated dicarboxylic acid, such as an anhydride of the acid, lower alkyl ester, fumaric acid, maleic acid, citraconic acid, and itaconic acid, or an anhydride of those, and lower alkyl ester, and a derivative of those are mentioned.

[0110]An alcohol component more than trivalent [which is committed also as a bridge construction ingredient] and an acid component more than trivalent can be used together.

[0111]As a polyhydric alcohol component more than trivalent [in this invention 1], Sorbitol, 1,2,3,6-hexane tetrol, 1, 4-sorbitan, Pentaerythritol, dipentaerythritol, tripentaerythritol, 1,2,4-butanetriol, 1 and 2, 5-pantanetriol, A polyhydric alcohol class more than trivalent [of glycerol, isobutane triol, 2-methyl-1,2,4-butanetriol, trimethylethane, trimethylolpropane, 1,3,5-trihydroxy benzene, etc.] is mentioned.

[0112]As a polyvalent carboxylic acid component more than trivalent [in this invention 1], Trimellitic acid, pyromellitic acid, 1,2,4-benzenetricarboxylic acid, 1,2,5-benzene tricarboxylic acid, 2,5,7-naphthalene tricarboxylic acid, 1,2,4-naphthalene tricarboxylic acid, 1,2,4-butane tricarboxylic acid, 1,2,5-hexane tricarboxylic acid, 1,3-dicarboxyl 2-methyl-2-methylenecarboxypropane, Tetra(methylenecarboxyl) methane, 1,2,7,8-octanetetracarboxylic acid, ene ball trimer acid and these anhydrides, lower alkyl ester; following formula [0113]

[Formula 3]



Polyvalent carboxylic acid and the derivatives of those, such as these anhydrides, such as tetracarboxylic acid expressed with (the alkylene group or alkenylene group of the carbon numbers 5–30 in which X in a formula has one or more with a carbon numbers of three or more side chains), and lower alkyl ester, are mentioned.

[0114]On the other hand, the THF insoluble matter of the binding resin used for the toner of this invention 3 is 20 or more (preferably 25 to 70 weight section) weight sections to binding resin 100 weight section. In the molecular weight distribution of THF extractives, in GPC chromatogram, a molecular weight has at least one peak to 2,000 or more and less than (still more preferably 3,000–12,000) 15,000 field preferably, And a molecular weight has a peak or at least one shoulder to the field of 15,000–100,000 (still more preferably 20,000–70,000).

[0115]A gap with a peak which is in 2,000 or more molecular weights thru/or less than 15,000 field still more preferably, a peak in a field of the molecular weights 15,000–100,000, or a shoulder is good for there to be a with a molecular weights of 10,000 or more difference often [that there is a with a molecular weights of 5,000 or more difference] and more preferably.

[0116]Even if THF insoluble matter in a resin composition performs refining of THF insoluble matter like this invention 3 in 70 or more weight sections for the melting characteristic, a rise of fixing temperature is caused and, as for these reasons, distribution of an additive agent worsens. Cutting of a viaduct region ingredient takes place easily at the time of resin kneading, and it becomes a cause which interferes with a design of a toner. As for blocking resistance at 50 **, less than 20 weight sections are not [that it is easy to produce offset in a low speed machine] enough as THF insoluble matter.

[0117]A peak value does not have a molecular weight of a THF solvent soluble component in 2,000 or more and less than 15,000 field, fixing temperature of a toner produced as a peak value is 15,000 or more rises, a fixing temperature region becomes narrow, grindability also gets worse, and decline in productive efficiency is caused. When a molecular weight of a peak value is less than 2,000, offset-proof nature may get remarkably bad, and a problem may produce a produced toner in blocking. If another peak or a molecular weight of a shoulder is not in 15,000–100,000 and the value exceeds 100,000, the dispersibility of an additive agent will be bad, and fixing temperature will also rise remarkably, and also grindability will also get worse remarkably. It is because offset-proof nature may worsen and a toner which a molecular weight of this peak or a shoulder produced by less than 15,000 may produce a problem in blocking.

[0118]a low molecular weight polymer and the amount polymer of polymers -- a weight ratio -- 5:95–70:30 -- it is good to exist by 10:90–50:50 preferably.

[0119]This is because offset-proof nature and blocking resistance are insufficient if grindability brings about evil of generating of coarse powder bad by less than five and a rate of a low molecular weight polymer exceeds 70.

[0120] T_g of a toner of this invention 3 is in the range of 45–65 **, and it is preferred that a ratio of a total content (M_s) of a styrene system monomer in THF insoluble matter of binding resin to a total content (M_a) of an acrylic system monomer is $1.0 \leq (M_s/M_a) < 2.5$. In $M_s/M_a < 1.0$, even if it increases quantity of THF insoluble matter, blocking resistance at 50 ** gets worse. $M_s/M_a > 2.5$ is not enough as low temperature fixability. $1.0 < (M_s/M_a) < 2.0$ is still more preferably good.

[0121]furthermore -- between ratios (M_{s_2}/M_{a_2}) of a total content (M_{s_2}) of a styrene system monomer in THF extractives, and a total content (M_{a_2}) of an acrylic system monomer -- $(M_s/M_a) > (M_{s_2}/M_{a_2})$ -- it is preferred that it is related. $(M_s/M_a) \leq (M_{s_2}/M_{a_2})$ of blocking resistance at 50 ** is insufficient even if it increases quantity of THF insoluble matter within the limits of the above (M_s/M_a).

[0122]It is defined as THF insoluble matter with a value measured as follows here.

[0123]Namely, only in the case of resin, a sample carries out weighing of a constant rate of resin (0.5–1.0g) (W_1 g), Put into an extraction thimble (Toyo Roshi No.86R), and it applies to Soxhlet

extractor, After evaporating a soluble component which extracted for 6 hours, using 100–200 ml of THF(s) as a solvent, and was extracted with a solvent, vacuum drying is carried out at 100 ** for several hours, weighing of the amount of meltable resinous principles is carried out (W_2 g), and it calculates according to the following formulas.

[0124]

$$\text{THF insoluble matter} = (W_1 - W_2)/W_1 \times 100 (\%)$$

When a sample is a toner, although a series of extract operation is the same as a case of resin, with nonmagnetic toner paints weight from sample toner weight, In magnetic toner, it is calculable according to a following formula from weight (W_3 g) which put and subtracted paints, magnetic body weight, etc. from sample toner weight, and solvent soluble component weight (W_4 g) in a toner.

[0125]

$$\text{THF insoluble matter} = (W_3 - W_4)/W_3 \times 100 (\%)$$

After it makes it dissolve in THF and an evaporation-to-dryness thing of a solvent soluble component obtained by the above operation passes a sample processing filter, let it be a sample of GPC.

[0126]In this invention 3, a peak of a chromatograph by GPC or/and a molecular weight of a shoulder are measured on the following conditions.

[0127]That is, a column is stabilized in a 40 ** heat chamber, in a column at this temperature, THF is passed at the rate of flow of 1 ml/m as a solvent, and 50–200microl pouring of the THF sample solution of resin adjusted to 0.05 to 0.1% of the weight as sample concentration is carried out, and it is measured. In the determination of molecular weight of a sample, molecular weight distribution which a sample has was computed from a relation of an opposite numerical value of an analytical curve and a count number which were produced by several sorts of monodisperse polystyrene standard samples. As a standard polystyrene sample for analytical curve creation, For example, A molecular weight by pressure chemical company make or an Oriental soda industrial company 6×10^2 , 2.1×10^3 , 4×10^3 , 1.75×10^4 , 5.1×10^4 , 1.1×10^5 , 3.9×10^5 , It is appropriate to use a standard polystyrene sample of about at least ten points using a thing of 8.6×10^5 , 2×10^6 , and 4.48×10^6 . RI (refractive index) detector is used for a detector.

[0128]In order to measure accurately a molecular weight region of 10^3 – 2×10^6 as a column, Combining more than one a commercial polystyrene gel column well. For example, mu made from Waters (Waters) – Combination of SUCHIRAGERU(styragel)500, 10^3 , 10^4 , and 10^5 , Shodex (Shodex)KF-80M by Showa Denko K.K., and combination of KF-802,803,804,805, Combination of combination of KA-802,803,804,805 or TSKgelG1000H made from Oriental soda, G2000H, G2500H, G3000H, G4000H, G5000H, G6000H, G7000H, and GMH is desirable.

[0129]When binding resin of this invention 3 raises blocking resistance and offset-proof nature further as for having the acid value of 1–70 in THF insoluble matter and/or THF extractives, it is preferred.

[0130]The following are mentioned as a polymerization nature monomer containing an acid radical which can be used for this invention 3.

[0131]alpha like acrylic acid and methacrylic acid, beta-unsaturation carvone acids; Maleic acid, alpha like maleic acid butyl, maleic acid octyl, fumaric acid, and fumaric acid butyl, beta-unsaturated dicarboxylic acid, or half ester;n-buteneylsuccinic acid of those, Alkenyl dicarboxylic acid or the half ester of those, such as n-octenylsuccinic acid, n-buteneylsuccinic acid butyl, n-buteneylmalonic acid, and n-buteneyladipic acid, etc. are mentioned. The desirable dicarboxylic acid in which no hydrating is possible, and a derivative of those are good.

[0132]in this case -- a polymerization nature monomer amount which contains an acid radical to binding resin entire volume has one to 30 preferred weight section -- as the acid value of the whole binding resin -- 1–70 -- 5–50 are still more preferably good.

[0133]Although stated in detail as a reason a half ester monomer of the above dicarboxylic acid is chosen later, it is because a suspension polymerization method is preferred as a

manufacturing method of resin. It is because it is not appropriate to use it in a form of an acid monomer with high solubility to suspension of a drainage system in this suspension polymerization and it is preferred to use in a form of ester with low solubility. A carboxylic acid system monomer in this invention 3 goes into neither of a styrene system monomer and an acrylic system monomer of the inside, but is excepted from calculation of a weight ratio of a styrene system monomer and an acrylic system monomer.

[0134]As a styrene system monomer which makes binding resin of this invention 3, for example, styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-methoxy styrene, p-phenylstyrene, p-KURORU styrene, 3,4-dichloro styrene, p-ethylstyrene, 2,4-dimethylstyrene, p-n-butylstyrene, p-tert-butylstyrene, p-n-hexylstyrene, p-n-octylstyrene, There are styrene, such as p-n-nonylstyrene, p-n-decylstyrene, and p-n-dodecylstyrene, and a derivative of those. As an acrylic system monomer, methyl methacrylate, ethyl methacrylate, Methacrylic acid propyl, n-butyl methacrylate, methacrylic acid isobutyl, N-octyl methacrylate, methacrylic acid dodecyl, methacrylic acid-2-ethylhexyl, Stearyl methacrylate, methacrylic acid phenyl, dimethylaminoethyl methacrylate, alpha-methylene aliphatic-monocarboxylic-acid ester species, such as diethylaminoethyl methacrylate; Methyl acrylate, ethyl acrylate, acrylic acid n-butyl, isobutyl acrylate, acrylic acid propyl, acrylic acid n-octyl, acrylic acid dodecyl, Acrylic ester; such as 2-ethylhexyl acrylate, acrylic acid stearyl, acrylic acid 2-KURORU ethyl, and acrylic acid phenyl, is used.

[0135]Rather than the above-mentioned styrene system and an acrylic system monomer, in a small quantity Ethylene, Unsaturation polyenes, such as ethylene unsaturation monoolefins; butadiene, such as propylene, butylene, and isobutylene; VCM/PVC, Vinylic halide, such as a vinylidene chloride, vinyl bromide, and **-ized vinyl; Vinyl acetate, Vinyl ester, such as vinyl propionate and BENZOE acid vinyl; Vinylmethyl ether, Vinyl ether, such as vinylethyl ether and vinyl isobutyl ether; Vinyl methyl ketone, Vinyl ketone;N-vinylpyrrole, such as vinyl hexyl ketone and methyl isopropenyl ketone, N-vinyl compound; vinylnaphthalene, such as N-vinylcarbazole, N-vinylindole, and N-vinyl pyrrolidone; monomers, such as acrylic acid, such as acrylonitrile, a methacrylonitrile, and acrylamide, or methacrylic acid derivative;, may be used together.

[0136]Binder resin used for this invention 3 needs to be the polymer over which the bridge was constructed by a cross-linking monomer which is illustrated below, in order to attain the purpose of this invention.

[0137]An aromatic divinyl compound, for example, divinylbenzene, divinylnaphthalene, etc.; The diacrylate compounds connected with an alkyl chain. For example, ethylene glycol diacrylate, 1,3-butylene-glycol diacrylate, 1,4-butanediol diacrylate, 1, 5-pentanediol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, And a thing which replaced acrylate of the above compound with methacrylate; The diacrylate compounds connected with an alkyl chain including an ether bond. For example, diethylene glycol diacrylate, triethylene glycol diacrylate, Tetraethylene glycol diacrylate, polyethylene-glycol #400 diacrylate, Polyethylene-glycol #600 diacrylate, dipropylene glycol diacrylate, And a thing which replaced acrylate of the above compound with methacrylate; The diacrylate compounds, for example, polyoxyethylene (2)-2,2-bis(4-hydroxyphenyl)propane diacrylate, connected with a chain including an aromatic group and an ether bond. What replaced polyoxyethylene (4)-2,2-bis(4-hydroxyphenyl)propane diacrylate and acrylate of the above compound with methacrylate; the polyester type diacrylate compounds (Nippon Kayaku) MANDA, for example, a trade name, are mentioned further. and as a cross linking agent of many organic functions, [pentaerythritol doria] Trimethylol triacrylate, trimethylolpropane triacrylate, What replaced tetramethylolmethane tetraacrylate, oligoester acrylate, and acrylate of the above compound with methacrylate; triaryl cyanurate and triallyl trimellitate; etc. are mentioned.

[0138]As for these cross linking agents, it is preferred to use to 100 % of the weight of other monomer components about (about further 0.03 to 3 % of the weight) 0.01 to 5% of the weight.

[0139]The diacrylate compounds connected with a chain including an aromatic divinyl compound (especially divinylbenzene), an aromatic group, and an ether bond to resin for toners among these cross-linking monomers as what is suitably used from a point of fixability and offset-proof nature are mentioned.

[0140]The synthesizing method of binder resin in connection with this invention 3 can control a weight ratio of a styrene system monomer in THF insoluble matter and extractives, and an acrylic system monomer by a method of compounding two or more sorts of polymers fundamentally.

[0141]That is, THF insoluble matter is the method of dissolving few [and] low molecular weight polymers meltable to polymerization monomers in polymerization monomers, polymerizing a monomer, and obtaining a resin composition. In this case, a constituent which a polymer of the former and the latter is mixing uniformly is formed.

[0142]A low molecular weight polymer in a binder resin constituent used for this invention 3 can be obtained by the polymerizing methods usually used, such as a mass polymerization method and a solution polymerization method.

[0143]Although a polymer of low molecular weight can be obtained in a mass polymerization method by making it polymerize at an elevated temperature and bringing termination reaction speed forward, there is a problem of being hard to control a reaction. In that respect, for obtaining a low molecular weight body in a resin composition which can obtain a low molecular weight polymer easily on mild conditions by adjusting the amount of initiators, and reaction temperature by a solution polymerization method, using a difference of radical chain transfer by a solvent, and is used by this invention 3, it is desirable.

[0144]As a solvent used by solution polymerization, xylene, toluene, a cumene, cellosolve acetate, isopropyl alcohol, benzene, etc. are used. In the case of a styrene monomer, xylene, toluene, or a cumene is preferred. It is suitably chosen by polymer which carries out polymerization generation. An initiator Di-tert butyl peroxide, tert-butylperoxy benzoate, Benzoyl peroxide, 2,2'-azobisisobutyronitrile, 2, and 2'-azobis (2, 4 dimethylvaleronitrile) etc. are used to monomer 100 weight section by concentration of 0.1 or more (preferably 0.4 to 15 weight section) weight sections. Although it changes as reaction temperature with a solvent and an initiator to be used, and polymerizing polymer, it is good to carry out at 70 ** - 180 **. It is preferred to carry out by monomer 30 weight section - 400 weight sections to solvent 100 weight section in solution polymerization.

[0145]This low molecular weight polymer has an emulsion polymerization method and a preferred suspension polymerization method as the polymerizing method for obtaining a gel component of a bridge construction region although it polymerizes again with a monomer which gives the amount polymer of polymers, until it becomes a solvent with an insoluble element.

[0146]Among these, an emulsion polymerization method is the method of making water distribute an almost insoluble monomer (monomer) in aqueous phase as small particles with an emulsifier, and polymerizing using a water-soluble polymerization initiator. By this method, regulation of reaction fever is easy, since a phase (oil phase which consists of a polymer and a monomer) and aqueous phase to which a polymerization is performed are another, termination reaction speed is small, as a result, a rate of polymerization is large, and a high-polymer thing is obtained. Since a polymerization process's being comparatively easy and a polymerization product are microscopic particles, in manufacture of a toner, there is an advantageous point as a manufacturing method of binder resin for toners from reasons mixing with colorant and a charge controlling agent, and other additives is easy etc.

[0147]However, a formed polymer becomes impure easily for an added emulsifier, operation of curing salting etc. is required to take out a polymer, and suspension polymerization is convenient in order to avoid this inconvenience.

[0148]On the other hand, while shape is ready in the shape of a pearl when a monomer having contained a low molecular weight polymer in which a suspension polymerization method became suspended state voice polymerizes with a cross linking agent, and a resin composition contains a bridge construction region ingredient from a low molecular weight polymer, where [desirable] even the amount polymer of polymers is mixed uniformly, it can be obtained.

[0149]In suspension polymerization, it is good to carry out to drainage system solvent 100 weight section by 100 or less (preferably ten to 90 weight section) weight section of monomers.

Although polyvinyl alcohol, a polyvinyl alcohol partial saponification thing, calcium phosphate, etc. are used and there is an adequate amount with a monomer amount to a drainage system solvent,

etc. as an usable dispersing agent, generally it is used by 0.05 to 1 weight section to drainage system solvent 100 weight section. Although 50-95 ** is suitable for polymerization temperature, it should choose suitably by an initiator to be used and polymer made into the purpose. Although it is possible to use if insoluble to water or refractory as an initiator kind, benzoyl peroxide, tert-butylperoxy hexanoate, etc. are used by 0.5 to 10 weight section to monomer 100 weight section, for example.

[0150]Although a method described above is a manufacturing method of binder resin used for this invention 3, a case where three sorts of resin which constitutes this binder resin is mixed in the time of melt kneading, etc. not using the above-mentioned polymerizing method is considered. At this time, distribution of each ingredient in binder resin becomes a problem. If it is within the limits of a predetermined compounding ratio, do not have big influence on molecular weight distribution of dispersibility or the whole binder resin, but. When a predetermined compounding ratio is changed so that quantity of THF insoluble matter of a vinyl system copolymer (B) may be increased for a reason on an offset-proof [which increases quantity of a vinyl system copolymer (A) for improvement in grindability] disposition or it may say that quantity of polyester resin is increased for improvement in fixable, it is easy to produce a maldistribution.

[0151]As coloring material which can be added further, paints or a color like publicly known carbon black and a copper phthalocyanine, etc. can be conventionally used for magnetic toner concerning this invention.

[0152]Magnetic toner of this invention may contain a charge controlling agent if needed, and, in the case of a negative triboelectric charging toner, negative charge controlling agents, such as a metallic complex of a metallic complex of a monoazo color, salicylic acid, alkyl salicylic acid, dialkyl salicylic acid, or naphthoic acid, are used.

[0153]In the case of a positive triboelectric charging toner, a positive charge control agent like a nigrosine series compound and organic quarternary ammonium salt is used.

[0154]To magnetic toner of this invention, it is preferred that a non-subtlety granular material or hydrophobic inorganic matter pulverized coal is mixed. For example, it is preferred to add and use silica impalpable powder.

[0155]Although it is [pulverized coal / which is used for this invention / silica] usable in both what is called wet process silica manufactured from dry process silica, water glass, etc. which are called what is called a dry method or fumed silica generated by vapor-phase oxidation of a silicon halogenated compound, There are few silanol groups in the surface and an inside, and the dry process silica without manufacture residue is more preferred.

[0156]Silica pulverized coal furthermore used for this invention has that preferred by which hydrophobing processing is carried out. In order to carry out hydrophobing processing, it is given by processing chemically with silica pulverized coal, a reaction, or an organic silicon compound that carries out physical adsorption. A method of processing with an organic silicon compound like silicone oil is mentioned after processing dry-process-silica pulverized coal generated by vapor-phase oxidation of a silicon halogenated compound by a silane coupling agent as a desirable method, or at the same time it processes by a silane coupling agent.

[0157]As a silane coupling agent used for hydrophobing processing, For example, hexamethyldisilazane, trimethylsilane, a trimethyl KURORU silane, Trimethylethoxysilane, a dimethyl dichloro silane, methyltrichlorosilan, An allyldimethyl KURORU silane, an allylphenyl dichloro silane, a benzylidimethyl KURORU silane, Bromine methyldimethyl KURORUSHIRAN, alpha-KURORU ethyl trichlorosilan, beta-KURORU ethyl trichlorosilan, KURORUMECHIRU dimethyl KURORUSHIRAN, Tori ORGANO Silang mercaptan, trimethylsilyl mercaptan, Tori ORGANO silylacrylate, vinylidimethyl acetoxy silane, A dimethylethoxy silane, dimethyldimethoxysilane, diphenyl diethoxysilane, hexamethyl disiloxane, 1,3-divinyl tetramethyl disiloxane, and 1,3-diphenyl tetramethyl disiloxane are mentioned.

[0158]Silicone oil is mentioned as an organic silicon compound. As desirable silicone oil, a thing of about 30 to 1,000 centistokes is used for viscosity at 25 **, For example, dimethyl silicone oil, methylphenyl silicone oil, alpha-methylstyrene modified silicone oil, KURORU phenyl silicone oil, fluoride modified silicone oil, etc. are preferred.

[0159]A method of silicone oil processing is good also by a method of injecting silicone oil to silica which may mix directly silica pulverized coal and silicone oil which were processed by a silane coupling agent using mixers, such as a Henschel mixer, and serves as a base. Or after making a suitable solvent dissolve or distribute silicone oil, silica pulverized coal of a base may be mixed, and a solvent may be removed and produced.

[0160]In magnetic toner in this invention, external additives other than silica pulverized coal may be added if needed.

[0161]For example, they are a resin particulate and inorganic particles which commit an electrification adjuvant, an electro-conductivity applying agent, a fluid grant agent, a caking inhibitor, a release agent at the time of hot calender roll fixing, lubricant, abrasive soap, etc.

[0162]A non-subtlety granular material mixed with magnetic toner or hydrophobic inorganic matter pulverized coal is good to carry out 0.1–5 weight-section (preferably 0.1 to 3 weight section) use to magnetic toner 100 weight section.

[0163]Magnetic toner for developing an electrostatic charge image concerning this invention to produce Magnetic powder and a vinyl system, Thermoplastics of a non-vinyl system, and if needed Paints or a color as colorant, After mixing a charge controlling agent, other additive agents, etc. enough with a mixer like a ball mill, a heating roller, Can use a heat kneading machine like a kneader and an extruder, paints or a color is made to be able to distribute or dissolve into [milled and resin was made to dissolve mutually] fusion and kneading, and magnetic toner which performs grinding after cooling solidification and a strict classification, and is applied to this invention can be obtained.

[0164]A magnetic oxide of iron which has a silicon element concerning this invention is manufactured, for example by a following method.

[0165]After adding a silicic acid compound of the specified quantity to a ferrous salt aqueous solution, alkali like sodium hydroxide more than the equivalent or the equivalent is added to a ferrous component, and solution containing ferrous hydroxide is prepared. Air is blown maintaining the pH of prepared solution or more to pH seven (preferably pH 8–10), ferrous hydroxide is oxidized, warming solution at not less than 70 **, and seed crystal used as a core of magnetic-oxide-of-iron particles is generated first.

[0166]Next, solution which contains about 1 Eq of ferrous sulfate in liquid of slurry form containing seed crystal on the basis of an addition of alkali added before is added. Blowing air maintaining the pH of liquid to 6–10, a reaction of ferrous hydroxide is recommended, seed crystal is used as a core, and magnetic-oxide-of-iron particles are grown up. The pH of liquid shifts to the acidity side as oxidation reaction progresses, but it is more desirable not to make the pH of liquid into less than six. By adjusting the pH of liquid to a telophase of oxidation reaction, it is preferred on a surface and the surface of magnetic-oxide-of-iron particles to carry out the specified quantity maldistribution of the silicic acid compound.

[0167]Silicic acid, such as sol-like silicic acid which produces a silicic acid compound used for addition in silicates, such as commercial sodium silicate, hydrolysis, etc., is illustrated. Unless it has an adverse effect on this invention, other additive agents, such as sulfuric acid aluminum and alumina, may be added.

[0168]As ferrous salt, use of ferrous sulfate which generally carries out a byproduction to sulfuric acid method titanium production, and ferrous sulfate which carries out a byproduction in connection with surface washing of a steel plate is possible, and also ferric chloride etc. are possible.

[0169]Iron concentration of 0.5–2 mol/l. is used from that a manufacturing method of a magnetic oxide of iron by a solution method generally prevents a rise of viscosity of reaction time, and solubility of ferrous sulfate. Concentration of ferrous sulfate has the tendency for a particle size of a product to become fine, so that it is generally thin. When reacting, it is easy to microatomize, so that reaction temperature is so low that there are many air contents.

[0170]It is preferred to comprise a spherical particle formed on a curved surface where magnetic-oxide-of-iron particles which have a silicic acid ingredient do not mainly have a tabular plane by observation by a transmission electron microscope photograph with an above-mentioned manufacturing method, to generate a magnetic oxide of iron which hardly contains

octahedron particles, and to use the magnetic oxide of iron for a toner.

[0171]An image forming device, a device unit, and a facsimile machine for using magnetic toner of this invention are explained.

[0172]One desirable example of an image forming device is explained referring to drawing 3.

[0173]The OPC photo conductor 3 surface is charged in negative polarity with the primary charging machine 11, and a digital latent image is formed by image scanning by the exposure 5 by a laser beam. Reversal development of this latent image is carried out by the one component system magnetic developer 13 which has magnetic toner of the developer 1 possessing the developing sleeve 6 which has included the elastic blade 9 and the magnet 15 of urethane rubber nature which were installed in a counter direction. In a developing section, mutual bias, pulse bias, and/or DC bias are impressed by the bias applying means 12 between a conductive base of the photoconductive drum 3, and the developing sleeve 6. The transfer paper P is conveyed, and if it comes to a transfer section, electrostatic image transfer of the developed image (toner image) on the photoconductive drum surface will be carried out on the transfer paper P by carrying out corona electrical charging from the back (the photoconductive drum side and an opposite side) of the transfer paper P by the electrostatic transfer means 4. Since a toner image on the transfer paper P is established by the heat pressing roller fixing assembly 7, fixing treatment of the transfer paper P separated from the photoconductive drum 3 is carried out.

[0174]A one component system developer which remains to a photoconductive drum after a transfer process is removed by the cleaning machine 14 which has the cleaning blade 8. The photoconductive drum 3 after cleaning is discharged by the IRESU exposure 19, and a process of beginning from an electrifying process with the primary charging machine 11 is repeated again.

[0175]An electrostatic charge image supporter (photoconductive drum) has a photosensitive layer and a conductive base, and moves to an arrow direction. The developing sleeve 6 of a nonmagnetic cylinder which is toner support rotates so that it may progress in the electrostatic image supporter surface and the direction in a developing section. It is allotted to an inside of the developing sleeve 6 of a nonmagnetic cylinder so that the multi-electrode permanent magnet 15 (magnet roll) which is a magnetic field generating means may not rotate. The one component system insulation developer 13 in the developer 1 is applied on a nonmagnetic cylinder side, and, as for a magnetic toner particle, a TORIBO electric charge of minus is given by friction with the surface of the developing sleeve 6, and a magnetic toner particle. By furthermore arranging the elastic doctor blade 9, thickness of a developer layer is regulated thinly (30 micrometers – 300 micrometers) and uniformly, and a developer layer thinner than a gap of the photoconductive drum 3 in a developing section and the developing sleeve 6 is formed so that it may become non-contact. It is made for sleeve surface speed to turn into speed of an electrostatic image buildup area with speed near *** or it substantially by adjusting revolving speed of this sleeve 6.

[0176]In a developing section, AC bias or pulse bias may be impressed by the bias means 12 between the sleeve 6 and the photoconductive drum 3. As for this AC bias, it is preferred that f is 200–4,000 Hz and Vpp(s) are 500–3,000V.

[0177]A magnetic toner particle is transferred to the electrostatic image side when transferring a magnetic toner particle in a developing section by operation of electrostatic power of the surface of the photoconductive drum 3 and AC bias holding an electrostatic image, or pulse bias.

[0178]Other examples of an image forming device of this invention are explained referring to drawing 4.

[0179]An image forming device shown in drawing 4 is different from an image forming device shown in drawing 3 with a point which has regulated thickness of a magnetic developer on the developing sleeve 6 with the magnetic doctor blade 16. In drawing 4, a member of the same reference number as drawing 3 shows the same member.

[0180]By approaching a cylindrical surface (50 micrometers – 500 micrometers of intervals), countering one magnetic pole position of a multi-electrode permanent magnet, and arranging iron doctor blades as the magnetic doctor blade 16, for example, Thickness of a developer layer is regulated thinly (30 micrometers – 300 micrometers) and uniformly, and a developer layer thinner

than a gap of the electrostatic charge image support 1 in a developing section and the developing sleeve 2 is formed so that it may become non-contact. It is made for sleeve surface speed to turn into speed of an electrostatic image buildup area with speed near *** or it substantially by adjusting revolving speed of this developing sleeve 2. A permanent magnet may be used instead of iron as the magnetic doctor blade 6, and opposing magnetic poles may be formed.

[0181]As an electrophotography device, it may combine with one, and may constitute by using two or more things as a device unit among components, such as electrostatic latent image support like an above-mentioned photoconductive drum, a developer, a cleaning means, and this unit may be constituted to a device main frame, enabling free attachment and detachment. For example, in support of at least one of an electrifying means, a developer, and the cleaning means, a unit may be formed in one with a photoconductive drum, and it may be considered as a single unit which can be freely detached and attached to a device main frame, and may have composition which can be detached and attached freely using guide mechanisms, such as a rail of a device main frame. At this time, it may constitute with an electrifying means and/or a developer in a way of the above-mentioned device unit.

[0182]Drawing 5 shows one example of a device unit of this invention. In this example, an image forming device of an electrophotographing system provided with the image formation unit (what is called a cartridge) 18 which made one the developer 1, the drum-like latent image support (photo conductor drum) 3, the cleaner 14, and the primary charging machine 11 is illustrated.

[0183]In this device, when the magnetic developer 13 of the developer 1 in this image formation unit 18 is lost, it is exchanged for a new cartridge.

[0184]In this example, in order to form a predetermined electric field between the photo conductor drum 3 and the developing sleeve 6 and to carry out a developing process suitably at the time of development, using a one component system magnetic developer as the developer 13, distance between the photoconductive drum 3 and the developing sleeve 6 is dramatically important for the developer 1. In this example, it is considered as a 300-micrometer center, and it is measured and adjusted so that an error may be set to **30 micrometers.

[0185]The developer container 2 for the developer 1 of this invention shown in drawing 5 to accommodate the magnetic developer 13, The developing sleeve 6 which supports the magnetic developer 13 in the developer container 2 to a developing area which met the latent image support 3, and conveys it from the developer container 2, It is supported with the developing sleeve 6, and in order to regulate a magnetic developer conveyed to a developing area to prescribed thickness and to form a developer thin layer on this developing sleeve, it has the elastic blade 9.

[0186]Said developing sleeve 6 can be made into arbitrary structures. Usually, it comprises the nonmagnetic developing sleeve 6 which built in the magnet 15. The developing sleeve 6 can also be used as a cylindrical solid of revolution so that it may be illustrated. It is also possible to consider it as belt shape which carries out circulation movement. As the construction material, it is usually preferred that aluminum and SUS are used.

[0187]Said elastic blade 9 comprises an elastic plate formed with urethane rubber, silicone rubber, the rubber elastomer; phosphor bronze like NBR, the metal-elastic-bodies; polyethylene terephthalate like a stainless plate, and a resin elastic body like *****. The elastic blade 9 is contacted by the developing sleeve 6 with elasticity which the member itself has, and is fixed to the developer container 2 by the braid support member 10 which comprises a rigid body like iron. As for the elastic blade 9, it is preferred to contact a counter direction to a hand of cut of the developing sleeve 6 by the linear pressure 5 – 80 g/cm.

[0188]In using an image forming device of this invention as a printer of a facsimile, optical image exposure turns into exposure for printing received data. Drawing 6 shows an example in this case with a block diagram.

[0189]The controller 611 controls the image reading part 610 and the printer 619. The whole controller 611 is controlled by CPU617. Read data from an image reading part is transmitted to a distant office through the sending circuit 613. Data which received from a distant office is sent to the printer 619 through the receiving circuit 612. Predetermined image data is memorized by

image memory. The printer controller 618 is controlling the printer 619. 614 is a telephone. [0190]CPU617 performs decoding processing of picture information and a picture (picture information from a remote terminal connected via a circuit) received from the circuit 615 is stored in the image memory 616 one by one, after getting over in the receiving circuit 612. And if at least 1-page picture is stored in the memory 616, image recording of the page will be performed. CPU617 sends out 1 page of picture information which read picture information of one page and was decrypted by the printer controller 618 from the memory 616. It controls the printer 619 in order to perform picture information record of the **-JI, if the printer controller 618 is received [CPU618 to 1 page of picture information].

[0191]During record with the printer 619, CPU617 is receiving the next page.

[0192]As mentioned above, reception and record of a picture are performed.

[0193]It is preferred that they are 10 or more g/cm as a linear pressure as contact pressure of an electrostatic charge image supporter and a transfer means concerning this invention 4. About a linear pressure, it computes with a following formula.

[0194](Linear pressure) [g/cm] = (total pressure applied to a transfer member) [g] / (length contacted) [cm]

Inferior transfer according that revolving speed of an outer diameter of latent image support is [contact pressure] less than 10 g/cm in a not less than 35 mm/sec image formation method to conveyance Bure of a transfer member and a shortage of transfer current starts, and it is not desirable. They are 20 or more g/cm especially preferably.

[0195]As a transfer device used for this invention 4, a transfer roller which is looked at by drawing 9, or a transfer belt which is looked at by drawing 10 is mentioned. Drawing 9 is a schematic diagram of an important section of this typical kind of image forming device, a device of a graphic display is perpendicularly extended in space, and the cylindrical image support (henceforth a photo conductor) 21 which rotates in the direction of arrow A, and the conductive transfer roller 22 which contacts this are allocated.

[0196]A primary charging machine for electrifying the surface uniformly around the photo conductor 21, Light figures by which image modulation was carried out to this electrified surface, such as a laser beam and catoptric light from a manuscript, are projected, Although it is not necessary to say having allocated an exposure part which attenuates potential of the portion concerned and forms an electrostatic latent image, a development counter, and a member which needs after transfer for the cleaner and other image formation which removes residual toner which remains in the photo conductor surface, they are all omitted.

[0197]The transfer roller 22 consists of the rodding 22a and the conductive elastic layer 22b, and the conductive elastic layer 22b is built with an elastic body about volume resistance 10^6 , such as urethane, EPDM, etc. which distributed conducting materials, such as carbon, -10^{10} omega-cm. Bias is impressed to the rodding 22a by the constant voltage power supply 28.

[0198]Drawing 10 applies this invention 4 to a transfer belt. The support drive of the transfer belt 29 is carried out with the electric conduction roller 30. Application of pressure to a transfer roller is usually performed by pressurizing an end shaft carrier of the rodding 22a.

[0199]The surface of this invention of a latent image carrier is especially effective to an image forming device which is an organic compound.

[0200]When an adhesive property with binding resin contained in a toner when an organic compound forms a surface layer uses a homogeneous material at best especially, it is for a chemical combination to arise in a point of contact, and for transfer nature to fall.

[0201]As surface material of a latent image carrier used for this invention, although silicone resin, a vinylidene chloride, ethylene-vinyl chloride, styrene acrylonitrile, styrene-methylmethacrylate, styrene, polyethylene terephthalate, polycarbonate, etc. are mentioned, It is not limited to this and other monomers or copolymerization between illustration resin, a blend, etc. can be used.

[0202]Especially this invention has an effective diameter of the latent image support 21 to an image forming device of 50 mm or less.

[0203]In the case of a byway drum, even if it uses the same linear pressure, since curvature is

large, it is for concentration of a pressure to take place easily in a contact part. A belt photo conductor is also considered that there is the same phenomenon, and is effective also to an image forming device with a curvature radius [in a transfer section] of 25 mm or less.

[0204]Revolving speed of an outer diameter of latent image support is not less than 35 mm/sec, also in an image formation method using a contact transfer method, a magnetic developer used for this invention 4 which has the above-mentioned feature does not have inferior transfers, such as a "transfer middle omission", etc., and its image concentration is still higher and it gives a picture which was excellent in reproducibility.

[0205]Even when further prolonged copy or print-out is continued, holding high definition without a "transfer middle omission", "fogging", etc. can be continued.

[0206]

[Example]Hereafter, an example explains this invention concretely. Number of copies or % indicated in the example shows weight section or weight %.

[0207]First, the example of manufacture of the magnetic oxide of iron used for each example is shown. Among these, the examples 5-8 of manufacture are used in Examples 5-8 concerning this invention 2.

[0208](Example 1 of manufacture) After adding sodium silicate so that the content of a silicon element may be 1.8% to an iron element into ferrous sulfate solution, an 1.0-1.1-Eq caustic-alkali-of-sodium solution was mixed to iron ion, and the solution containing ferrous hydroxide was prepared.

[0209]Maintaining the pH of solution to pH 7-10 (for example, pH 9), air was blown, it oxidized at 80-90 **, and the slurry liquid which makes seed crystal generate was prepared.

[0210]Subsequently, after adding ferrous sulfate solution so that it may become this slurry liquid with 0.9-1.2 Eq to the original amount of alkali (the sodium ingredient of sodium silicate, and the sodium ingredient of caustic alkali of sodium), It maintained to pH 6-10 (for example, pH 8) of slurry liquid, and oxidation reaction was recommended, blowing air, pH was adjusted to the telophase of oxidation reaction, and the silicic acid ingredient was made unevenly distributed in a magnetic-oxide-of-iron particle surface. Crack processing of the particles which wash, filter, dry with a conventional method and are subsequently condensing the generated magnetic-oxide-of-iron particles was carried out, and the magnetic oxide of iron which has the characteristic as shown in Table 2 was obtained.

[0211]The data which measured the dissolved amount of the iron element and the silicon element every 10 minutes is shown in Table 1, and the relation of the dissolution rate of the iron element and silicon element of a magnetic oxide of iron is shown in drawing 1.

[0212]The content C of the silicon element of the silicon compound origin like the silicic acid eluted with the alkali which exists in the magnetic-oxide-of-iron particle surface C shown in drawing 2 in the magnetic oxide of iron obtained in the example 1 of manufacture is 17.9 mg/l, The content B of the silicon element of the silicon compound origin which exists in the magnetic-oxide-of-iron particle layer part B shown in drawing 2 was 38.8 mg/l, and the content A was 59.7 mg/l.

[0213]

[Table 1]

	溶 解 時 間 (分)											
	10	20	30	40	50	60	70	80	90	100	110	120
鉄元素溶解量 mg/1	335	635	1280	1790	2155	2450	2650	2885	3050	3215	3280	3315
鉄元素溶解率 重量%	10.1	19.2	38.6	54.0	65.0	73.9	79.9	87.0	92.0	97.0	98.9	100
ケイ素元素溶解量 mg/1	30.4	38.2	43.6	46.6	48.4	50.7	51.9	53.7	54.9	57.3	59.1	59.7
ケイ素元素溶解率 重量%	51	64	73	78	81	85	87	90	92	96	99	100

(Example 2 of manufacture) The magnetic oxide of iron which has the characteristic as shown in Table 2 like the example 1 of manufacture was obtained except having added sodium silicate so that it might become 2.9% about the content of the silicon element to an iron element in the example 1 of manufacture.

[0214](Example 3 of manufacture) The magnetic oxide of iron which has the characteristic as shown in Table 2 like the example 1 of manufacture was obtained except having added sodium silicate so that it might become 0.9% about the content of the silicon element to an iron element in the example 1 of manufacture.

[0215](Example 4 of manufacture) The magnetic oxide of iron which has the characteristic as shown in Table 2 like the example 1 of manufacture was obtained except having added sodium

silicate so that it might become 1.7% about the content of the silicon element to an iron element in the example 1 of manufacture.

[0216](Example 1 of comparison manufacture) The magnetic oxide of iron which has the characteristic as shown in Table 2 like the example 1 of manufacture was obtained except not adding sodium silicate in the example 1 of manufacture.

[0217](Example 2 of comparison manufacture) The magnetic oxide of iron which has the characteristic as mixed the silicic acid pulverized coal of 1.5 copies with a Henschel mixer and shown in Table 2 was obtained to 100 copies of magnetic oxides of iron obtained by the example 1 of comparison manufacture.

[0218]

[Table 2]

	ケイ素元素含有率(%)	(B/A) × 100	(C/A) × 100	帶電量(μc/g)	体積固有抵抗値(Ω・cm)	凝聚度(%)	BET比表面積(m ² /g)	平均粒径から計算したBET比表面積(m ² /g)	平滑度(D)	平均粒径(μm)	球形度(ϕ)
製造例1	1.8	65	30	-48	5×10^5	12	23.0	5.7	0.25	0.21	0.90
製造例2	2.9	57	25	-55	1×10^6	9	29.0	6.3	0.22	0.19	0.93
製造例3	0.9	83	42	-45	5×10^4	25	12.0	4.3	0.36	0.28	0.84
製造例4	1.7	52	18	-47	3×10^4	35	20.0	8.0	0.40	0.15	0.91
比較製造例1	0	-	-	-19	1×10^3	42	5.6	5.5	0.98	0.22	0.83
比較製造例2	約1.5%	ヘンシェル混合	-	100	-46	8×10^5	13	35.0	5.5	0.16	0.22
											0.83

(The examples 5-8 of manufacture, and examples 3-4 of comparison manufacture) After diluting silicone oil with methyl alcohol and mixing gently with a Henschel mixer further to the magnetic oxide of iron of the characteristic shown in said table 2, the alcohol content was volatilized and the magnetic oxide of iron which performed hydrophobing processing shown in Table 3 was obtained.

[0219]

[Table 3]

	使用した 磁性酸化鉄	疎水化処理
製造例5	製造例1	ジメチルシリコーンオイル (100ストークス) 0.3重量%
製造例6	製造例2	メチルフェニルシリコーン オイル (600ストークス) 5.0重量%
製造例7	製造例3	ジメチルシリコーンオイル (50ストークス) 0.06重量%
製造例8	製造例4	フッ素変性シリコーンオイル (150ストークス) 0.5重量%
比較製造例3	比較製造例1	ジメチルシリコーンオイル (1100ストークス) 8.0重量%
比較製造例4	比較製造例2	_____
(表中のシリコーンオイルの粘度は25°Cにおける値を示す。)		

Examples 1–4 are examples concerning this invention 1.

[0220] Example 1 and styrene maleic acid n-butyl-divinylbenzene copolymer 60 copies (Tg58 **, peak 200,000)

– Bisphenol A, terephthalic acid, n-dodecyl succinic acid 40 copies And polyester resin obtained from triethylene glycol (Tg56 **, Mn4,000, Mw35,000)
 – Magnetic oxide of iron of the example 1 of manufacture One copy of 100 copy and negative charge controlling agent (dialkyl-salicylic-acid system chromium complex), and low molecular weight polypropylene The three-copy above-mentioned mixture, Melt kneading was carried out by the biaxial extruder heated by 140 **, coarse grinding of the cooled kneaded material was carried out with the hammermill, the pulverizing powder obtained by pulverizing a coarse-grinding thing with a jet mill was classified with the fixed wall type pneumatic elutriation machine, and classification powder was generated. Classification removal of superfines and the coarse powder was simultaneously carried out strictly with the hyperfractionation classifier (elbow jet classifier by Nittetsu Mining Co., Ltd.) which used the Coanda effect for the obtained classification powder, and the negative triboelectric charging magnetic toner of 6.8 micrometers (0.2% of content of a magnetic toner particle with a particle diameter of 12.7 micrometers) of weight average particle sizes (D4) was obtained.

[0221] 1.2 copies of hydrophobic silica pulverized coal processed by silicone oil after carrying out hexamethyldisilazane treatment were mixed with 100 copies of this magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0222] It converted, as the device unit portion (toner cartridge) of commercial laser beam printer LBP-8II (made by Canon, Inc.) was shown in drawing 3, and the elastic blade made of urethane rubber was contacted by contact pressure 30 g/cm to the developing sleeve made from aluminum.

[0223] Use the above-mentioned magnetic developer, set primary charging to 700V, and the electrostatic latent image for reversal development is formed on the OPC photoconductive drum 3, A gap (300 micrometers) is set as the photoconductive drum 3 and non-contact for the developer layer on the developing sleeve 6 (magnet intension), Impressing AC bias (f= 1,800 Hz, V_{pp}=1,600V) and DC bias (V_{DC}=-500V) to a developing sleeve, V_L was set to -170V, the electrostatic charge image was developed by reversal development, and the magnetic toner image was formed on the OPC photo conductor. The formed magnetic toner image was transferred to the regular paper with plus transfer potential, and the magnetic toner image was established through the heat pressing roller fixing assembly in the regular paper which has a

magnetic toner image.

[0224]One by one, the image output test was done to 6000 sheets under ordinary temperature normal-relative-humidity environment (23.5 **, 60%RH), supplying a magnetic developer. The result of having done fogging computed from comparison with the image concentration measured with the Macbeth reflection density meter and the whiteness degree of the transfer paper after printing the whiteness degree and solid white of a transfer paper which were measured in RIFUREKU meter (made by Tokyo Denshoku Co., Ltd.), and the image output test which seems to be shown in drawing 7, and having seen dot reproducibility is shown in Table 4.

[0225]Similarly, the image output test was done under a high-humidity/temperature environment and low-humidity/temperature environment (32.5 **, 85%RH) (10 **, 15%RH). A result is shown in Table 4.

[0226]Example 2 and styrene 2 ethylhexyl acrylate 20 copies n-butyl acrylate divinylbenzene copolymer (Tg65 **, peak 1,900,000)

– bisphenol A, terephthalic acid, and trimellitic acid -- and -- 80 copies Polyester resin obtained from triethylene glycol (Tg54 **, Mn2,100, Mw7,000)

– Magnetic oxide of iron of the example 2 of manufacture 60 copy and negative charge controlling agent (monoazo color system chromium complex) 0.8 copy and low molecular weight polypropylene Melt kneading of the three-copy above-mentioned mixture is carried out by the biaxial extruder heated by 140 **, Coarse grinding of the cooled kneaded material was carried out with the hammermill, and this coarse-grinding thing was pulverized with the jet mill. Pneumatic elutriation of the obtained pulverizing powder was carried out, and the negative triboelectric charging magnetic toner of 11 micrometers (33% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes (D_4) was obtained.

[0227]0.6 copy of hydrophobic colloidal silica processed by dimethyl silicone oil was mixed with 100 copies of obtained magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0228]This magnetic developer was supplied to the device unit (toner cartridge) of laser beam printer LBP-8II, and the image output test was done like Example 1. A result is shown in Table 4.

[0229]Example 3 and styrene n-butyl acrylate copolymer 80 copies (Tg53 **, peak 8,000)

– Bisphenol A, terephthalic acid, n-dodecetyl succinic acid 20 copies And polyester resin obtained from triethylene glycol (Tg62 **, Mn7,300, Mw220,000)

– Magnetic oxide of iron of the example 3 of manufacture 120 copy and negative charge controlling agent (monoazo color system chromium complex) Two copy and low molecular weight polypropylene It is made to be the same as that of Example 1 using the three-copy above-mentioned material. The magnetic toner of 4 micrometers (0% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes (D_4) was obtained.

[0230]1.6 copies of hydrophobic colloidal silica processed by silicone oil was mixed with 100 copies of obtained magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0231]Several multi-sheet image output test was done like Example 1 using this magnetic developer. A result is shown in Table 4.

[0232]Example 4 and styrene 2 ethylhexyl acrylate copolymer 60 copies (Tg63 **, peak 60,000)

– Bisphenol A, terephthalic acid, n-dodecetyl succinic acid 40 copies It is obtained from trimellitic acid and triethylene glycol. Polyester resin (Tg56 **, Mn6,000, Mw60,000)

– Magnetic oxide of iron of the example 4 of manufacture One copy of 90 copy and negative charge controlling agent (dialkyl-salicylic-acid system chromium complex), and low molecular weight polypropylene It is made to be the same as that of Example 1 using the three-copy above-mentioned material. The magnetic toner of 8.5 micrometers (4% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes (D_4) was obtained.

[0233]One copy of hydrophobic colloidal silica pulverized coal processed by silicone oil after processing by hexamethyldisilazane was mixed with 100 copies of obtained magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0234]This magnetic developer was supplied to the device unit (toner cartridge) of the modified machine which converted laser beam printer LBP-8II so that it might become a part for 16-sheet/by the image output of the length of A4 copy paper, and the image output test was done like Example 1. A result is shown in Table 4.

[0235]Except for using the magnetic oxide of iron of the example 1 of comparative example 1 comparison manufacture, the magnetic toner of 7 micrometers (0.3% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes was obtained like Example 1. The image output test was done like Example 1 using the magnetic developer which prepared and prepared the magnetic developer like Example 1 using the obtained magnetic toner. A result is shown in Table 4.

[0236]Except for using the magnetic oxide of iron of the example 2 of comparative example 2 comparison manufacture, the magnetic toner of 8.7 micrometers (5% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes was obtained like Example 4. The image output test was done like Example 4 using the magnetic developer which prepared and prepared the magnetic developer like Example 4 using the obtained magnetic toner. A result is shown in Table 4.

[0237]

[Table 4]

	画像濃度			カブリ	ドット再現性	定着性	耐オフセット性
	常温常湿 初期	常温常湿 6000枚後	高温高湿 6000枚後	低温低湿 3000枚時	常温常湿		
実施例1	1.45	1.45	1.37	1.43	0.7 %	○	○
実施例2	1.41	1.43	1.40	1.41	1.1 %	○△	○
実施例3	1.41	1.40	1.36	1.40	1.3 %	○	○
実施例4	1.42	1.41	1.37	1.43	0.8 %	○	○
比較例1	1.39	1.05	1.00	1.08	7.0 %	××	○
比較例2	1.40	1.03	1.01	1.07	7.3 %	××	○

(a) Fogging was computed with the following formula.

[0238] If whiteness degree fogging of the whiteness degree-transfer paper of the transfer paper after a fogging (%) = solid white print is 1.5% or less, it is a good picture.

(b) Dot reproducibility did the image output test using the 80x50-micrometer checkered pattern shown in drawing 7, and the sharpness of a toner image and the toner to the nonimage area scattered, and it evaluated the existence of the deficit of a black part by the microscope.

(c) Fixability neglects one evening of evaluators under low temperature environment (10 **), The fixing assembly of an evaluator and its inside switched on the power supply from the state which adapted itself to environment thoroughly, printed out the horizontal line pattern (the line width of 200 micrometers, 200 micrometers of intervals) of 200-micrometer width immediately after the

weight rise, and used the printing image of the 1st sheet for fixable evaluation. Fixable evaluation rubbed the picture by 100g of five round trip load in SHIRUBON paper, and evaluated peeling of the picture by the decreasing rate (%) of reflection density.

(d) Offset-proof nature stopped the horizontal line pattern of 100-micrometer width for 30 seconds after a 300-sheet continuous print using a new fixing pad, started the print again, and evaluated it by the grade of next soiling on the back of paper of the 1st sheet.

[0239]A valuation basis is shown below.

1) Dot reproducibility O -- [-- 6-10 deficits/100 piece x / -- / -- The average concentration decreasing rate 0 - 5%** . / 11-20 deficits/100 piece xx -- 21 pieces more than/100 deficit 2 fixable O] Two or less deficit / 100 piece O** -- 3-5 deficits/100 piece ** -- The average concentration decreasing rate 5 - 8%x -- Not less than 10% of average concentration decreasing rate offset-proof [3] nature (after-pause soiling on the back of paper)

O -- [-- Although it is dirty, it is practical use good x. / -- Dirt is conspicuous and they are practical use improper 4 blocking resistance (50 ** three days).] O** which does not become dirty at all -- Hardly understood **

O -- [-- **x which will get loose if it pushes lightly, although an aggregate is seen / -- x which an aggregate is seen and cannot get loose easily / -- Examples 5-8 in which an aggregate is seen and does not get loose are examples concerning this invention 2.] Change-less O** -- ** which will get loose if it falls lightly, although an aggregate is seen

[0240]Example 5 and styrene 2-ethylhexyl acrylate 100 copies Maleic acid n-butyl half ester copolymer (the copolymerization weight ratio 7.5:1.5:1, Mw250,000)

- Magnetic oxide of iron of the example 5 of manufacture One copy of 100 copy and negative charge controlling agent (dialkyl-salicylic-acid system chromium complex), and low molecular weight polypropylene The three-copy above-mentioned mixture, Melt kneading was carried out by the biaxial extruder heated by 140 **, coarse grinding of the cooled kneaded material was carried out with the hammermill, the pulverizing powder obtained by pulverizing a coarse-grinding thing with a jet mill was classified with the fixed wall type pneumatic elutriation machine, and classification powder was generated. Classification removal of superfines and the coarse powder was simultaneously carried out strictly with the hyperfractionation classifier which used the Coanda effect for the obtained classification powder, and the negative triboelectric charging magnetic toner of 6.7 micrometers (0.2% of content of a magnetic toner particle with a particle diameter of 12.7 micrometers) of weight average particle sizes (D_4) was obtained.

[0241]1.2 copies of hydrophobic silica pulverized coal processed by silicone oil after carrying out hexamethyldisilazane treatment were mixed with 100 copies of this magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0242]The magnetic toner image was established in same electrification and developing condition using the image forming device shown in drawing 3 like Example 1.

[0243]One by one, the intermittent image output test which outputs one A4 over several days at 30 seconds under ordinary temperature normal-relative-humidity environment (23.5 **, 60%RH) was done, supplying a magnetic developer. The result of having seen fogging and dot reproducibility which were searched for like Example 1 is shown in Table 5.

[0244]Similarly, the intermittent image output test which outputs one A4 over several days at 30 seconds under a high-humidity/temperature environment and low-humidity/temperature environment (32.5 **, 90%RH) (10 **, 15%RH) was done. A result is shown in Table 5.

[0245]Example 6 and styrene n-butyl acrylate copolymer 100 copies (the copolymerization weight ratio 8:2, Mw280,000)

- Magnetic oxide of iron of the example 6 of manufacture 60 copy and negative charge controlling agent (monoazo color system chromium complex) 0.8 copy and low molecular weight polypropylene Melt kneading of the three-copy above-mentioned mixture is carried out by the biaxial extruder heated by 140 **, Coarse grinding of the cooled kneaded material was carried out with the hammermill, and this coarse-grinding thing was pulverized with the jet mill. Pneumatic elutriation of the obtained pulverizing powder was carried out, and the negative triboelectric charging magnetic toner of 11.1 micrometers (33% of content of a magnetic toner

particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes (D_4) was obtained.

[0246]0.6 copy of hydrophobic colloidal silica processed by dimethyl silicone oil was mixed with 100 copies of obtained magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0247]This magnetic developer was supplied to the device unit (toner cartridge) of laser beam printer LBP-8II, and the image output test was done like Example 5. A result is shown in Table 5.

[0248]Example 7 and styrene n-butyl acrylate 100 copies (the copolymerization weight ratio 8:2, Mw300,000)

– Magnetic oxide of iron of the example 7 of manufacture 120 copy and negative charge controlling agent (monoazo color system chromium complex) Two copy and low molecular weight polypropylene It is made to be the same as that of Example 5 using the three-copy above-mentioned material. The magnetic toner of 4.2 micrometers (0% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes (D_4) was obtained.

[0249]1.6 copies of hydrophobic colloidal silica processed by silicone oil was mixed with 100 copies of obtained magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0250]Several multi-sheet image output test was done like Example 5 using this magnetic developer. A result is shown in Table 5.

[0251]Example 8 and styrene n-ethylhexyl acrylate 100 copies Maleic acid n-butyl half ester copolymer (the copolymerization weight ratio 7.5:1.5:1, Mw250,000)

– Magnetic oxide of iron of the example 8 of manufacture One copy of 90 copy and negative charge controlling agent (dialkyl-salicylic-acid system chromium complex), and low molecular weight polypropylene It is made to be the same as that of Example 5 using the three-copy above-mentioned material. The magnetic toner of 8.5 micrometers (4% of content of a magnetic toner particle with a particle diameter of not less than 12.5 micrometers) of weight average particle sizes (D_4) was obtained.

[0252]One copy of hydrophobic colloidal silica pulverized coal processed by silicone oil after processing by hexamethyldisilazane was mixed with 100 copies of obtained magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0253]This magnetic developer was supplied to the device unit (toner cartridge) of the modified machine converted so that the length of A4 copy paper might **** laser beam printer LBP-8II and it might become a part for 16-sheet/, and the image output test was done like Example 5. A result is shown in Table 5.

[0254]Except for using the magnetic oxide of iron of the example 3 of comparative example 3 comparison manufacture, the magnetic toner of 6.9 micrometers (0.3% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes was obtained like Example 5. The image output test was done like Example 5 using the magnetic developer which prepared and prepared the magnetic developer like Example 5 using the obtained magnetic toner. A result is shown in Table 5.

[0255]Except for using the magnetic oxide of iron of the example 4 of comparative example 4 comparison manufacture, the magnetic toner of 8.8 micrometers (5.1% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes was obtained like Example 8. The image output test was done like Example 8 using the magnetic developer which prepared and prepared the magnetic developer like Example 8 using the obtained magnetic toner. A result is shown in Table 5.

[0256]The magnetic oxide of iron of the example 5 of comparative example 5 manufacture was used, the magnetic toner which has 14.1 micrometers (59% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes like Example 1 was obtained, the magnetic developer was prepared like Example 5, and the image output test was done like Example 5. A result is shown in Table 5.

[0257]As compared with the magnetic developer of Example 5, dot reproducibility was inferior and TOBICHIRI of the toner was also seen.

[0258]

[Table 5]

	画 像 濃 度				カブリ	ドット再現性
	常温常温 初期	常温常温 耐久終期	低温低温 耐久終期	高温高温 耐久終期		
実施例5	1.45	1.45 (7千枚)	1.42 (7千枚)	1.45 (7千枚)	1.41	0.9%
実施例6	1.43	1.43 (1.2万枚)	1.38 (1.2万枚)	1.44 (1.2万枚)	1.40	1.1% ○△ (1.2万枚)
実施例7	1.42	1.40 (7千枚)	1.38 (7千枚)	1.40 (7千枚)	1.38	1.5% ○ (7千枚)
実施例8	1.44	1.41 (1.2万枚)	1.40 (1.2万枚)	1.42 (1.2万枚)	1.39	0.7% ○ (1.2万枚)
比較例3	1.40	1.06 (7千枚)	1.00 (7千枚)	1.37 (7千枚)	1.35	8.0% × (7千枚)
比較例4	1.41	1.08 (1.2万枚)	1.02 (1.2万枚)	1.00 (1.2万枚)	0.80	6.6% × (1.2万枚)
比較例5	1.41	1.40 (7千枚)	1.20 (7千枚)	1.25 (7千枚)	1.22	1.1% × (7千枚)

Hereafter, the synthetic examples 1-4 are synthetic examples of the binding resin used for Examples 9-12.

[0259](Synthetic example 1)

- Styrene monomer 76 copy and acrylic acid n-butyl 14 copy and maleic acid monobutyl It was dropped into 200 copies of cumenes made to warm to flowing-back temperature, having applied

8 copies of ten-copy and di-tert-butyl peroxide above-mentioned each ingredient for 4 hours. Furthermore, solution polymerization was completed under cumene flowing back (146–156 **), and the cumene was removed. The molecular weight in which the main peak of GPC is located was 5,000, and Tg of obtained copolymer (I) was 60 **.

[0260]These 30 copies of copolymers were dissolved in the following monomeric mixture, and it was considered as the mixed solution.

– Styrene monomer 43 copy and acrylic acid n-butyl 15 copy and n-butyl methacrylate Nine copy and maleic acid monobutyl Three copy and divinylbenzene 0.35 copy and benzoyl peroxide To the 1.5-copy above-mentioned mixed solution, 0.1 copy of polyvinyl alcohol partial saponification thing. 170 copies of dissolved water was added and it was considered as suspension dispersion liquid. The above-mentioned suspension dispersion liquid were added to the reactor which put in and carried out the nitrogen purge of 15 copies of water, and the suspension polymerization reaction was carried out with the reaction temperature of 70–95 ** for 6 hours. The ** exception carried out after ending reaction, it dried and dried, and the constituent of a styrene acrylic acid n-butyl copolymer and a styrene acrylic acid n-butyl-methacrylic acid n-butyl-maleic acid monobutyl copolymer was obtained.

[0261]THF insoluble matter and THF extractives are mixing this constituent uniformly. And the styrene acrylic acid n-butyl copolymer and the styrene acrylic acid n-butyl-methacrylic acid n-butyl-maleic acid monobutyl copolymer were being mixed uniformly.

The number of the THF insoluble matter (it measures with 24 mesh passes and the granular material of 60-mesh one) of the obtained resin composition (A) was 45. When the molecular weight distribution of THF extractives was measured, in the chart of GPC, it had a peak in about 05500 position, and had a shoulder in about 34,000 position, Tg of resin was 59 **, and acid value was 18.6.

[0262]In this invention, the glass transition point Tg of resin and a toner was measured according to the ASTM D3418–82 method using a differential-thermal-analysis measuring device (DSC measurement device) and DSC-7 (made by PerkinElmer, Inc.).

[0263]A test portion carries out weighing of the 10 mg 5–20-mg precisely preferably.

[0264]This is put in aluminum bread, and after carrying out temperature up to 200 ** once and quenching, using empty aluminum bread as a reference, it measures under ordinary temperature normal relative humidity by the heating rate of 10 ** / min between 30 ** – 200 ** of measurement temperature requirements.

[0265]By this temperature rise process, the endothermic peak of the main peak in the range of 40–100 ** temperature is obtained.

[0266]It was considered as the intersection of the line of the halfway point of the baseline after coming out before the endothermic peak at this time comes out, and a differential thermal curve.

[0267]The acid value of resin was measured by the following method according to JIS K-0070.

[0268]Weighing of the samples 2–10g is carried out to a 200–300-ml Erlenmeyer flask, and, in addition, about 50 ml of mixed solvents of ethanol:benzene =1:2 dissolve resin. As long as it seems that solubility is bad, a small amount of acetone may be added. It titrated using the phenol FUTAREN indicator with N / 10 potassium hydrates by which standardization was carried out beforehand – an alcohol solution, and acid value was calculated in the following formula from the amount of consumption of alcoholic potassium liquid.

[0269]

Acid value = KOH(ml number) xNx56.1 / sample weight (however, N factor of N/10 KOH)
(Synthetic example 2)

– Styrene monomer 87 copy and acrylic acid n-butyl 13 copy and di-tert-butyl peroxide It was dropped into 200 copies of xylene made to warm to flowing-back temperature, having applied six-copy above-mentioned each ingredient for 4 hours. Furthermore, solution polymerization was completed under xylene flowing back (138–144 **), and xylene was removed. The molecular weight in which the main peak of GPC is located was 8,700, and Tg of obtained copolymer (II) was 61 **.

[0270]These 30 copies of copolymers were dissolved in the following monomeric mixture, and it

was considered as the mixed solution.

- styrene monomer 35 copy and 2-ethylhexyl acrylate . Ten copy and n-butyl methacrylate 15 copy and maleic acid monobutyl Ten copy and divinylbenzene 0.4 copy and benzoyl peroxide 170 copies of water which dissolved 0.1 copy of polyvinyl alcohol partial saponification thing in the 1.7-copy above-mentioned mixed solution was added, and it was considered as suspension dispersion liquid.

[0271]The above-mentioned dispersion liquid were added to the reactor which put in and carried out the nitrogen purge of 15 copies of water, and it was made to react to it with the reaction temperature of 70-95 ** for 6 hours. It dried and dried and the ** exception after ending reaction obtained the resin composition (B). The number of the THF insoluble matter of the obtained resin composition was 55. When the molecular weight distribution of THF extractives was measured, in the chart of GPC, it had a peak in about 09000 position, and had a shoulder in about 36,000 position, Tg of resin was 55.5 **, and acid value was 30.0.

[0272](Synthetic example 3)

- Styrene monomer 100 copy and di-tert-butyl peroxide 150 copies of cumenes were put into a 12-copy reactor, and temperature up was carried out to flowing-back temperature. The above-mentioned mixture was dropped over 4 hours under cumene flowing back. And the polymerization was completed under cumene flowing back (146-156 **), and the cumene was removed. Obtained polystyrene (III) had a main peak in the molecular weight 4,000, and Tg was 67 **. 40 copies of above-mentioned polystyrene was dissolved in the following monomeric mixture, and it was considered as the mixture.

- Styrene monomer 35 copy and acrylic acid n-butyl Ten copy and n-butyl methacrylate Ten copy and methyl methacrylate Five copy and divinylbenzene 0.4 copy and benzoyl peroxide Into the 1.3-copy above-mentioned mixture, 0.1 copy of polyvinyl alcohol partial saponification thing. 170 copies of dissolved water was added and it was considered as suspension dispersion liquid. The above-mentioned dispersion liquid were added to the reactor which put in and carried out the nitrogen purge of 15 copies of water, and it was made to react to it with the reaction temperature of 70-95 ** for 6 hours. It dried and dried and after ending reaction and a ** exception obtained the constituent of polystyrene and a styrene acrylic acid n-butyl-methacrylic acid n-butyl-methyl methacrylate copolymer.

[0273]The number of the THF insoluble matter of the obtained resin composition (C) was 60. When the molecular weight distribution of THF extractives was measured, in the GPC chart, it had a peak in about 04500 position, and had a shoulder in about 38,000 position, Tg of resin was 56 **, and acid value was 0.6.

[0274](Synthetic example 4) Except polymerizing by dissolving 30 copies of copolymer (III)s in the following monomeric mixture in the synthetic example 3, it carried out similarly and the copolymer composition thing was obtained.

- Styrene monomer 48 copy and acrylic acid n-butyl Ten copy and n-butyl methacrylate 12 copy and divinylbenzene 0.6 copy and benzoyl peroxide The number of the THF insoluble matter of the polymer composition (D) obtained 1.5 copies was 60. When the molecular weight distribution of THF extractives was measured, in the GPC chart, it had a peak in the molecular weight about 05400 position, and had a shoulder in about 37,000 position, and the acid value of Tg of resin was 1.2 at 65 **.

[0275](Example 1 of comparison composition) 200 copies of cumenes are put into a reactor, and temperature up is carried out to flowing-back temperature. The following mixture was dropped over 4 hours under cumene flowing back.

- Styrene monomer 75 copy and n-butyl methacrylate 25 copy and di-tert-butyl peroxide Six copies of polymerizations were further completed under cumene flowing back (146-156 **), and the cumene was removed. Obtained styrene acrylic acid n-butyl copolymer (IV) had a main peak in the position of the molecular weight 6,300, and Tg was 55 **.

[0276]30 copies of above-mentioned copolymers were dissolved in the following monomeric mixture, and it was considered as the mixture.

- Styrene monomer 55 copy and 2-ethylhexyl acrylate 15 copy and divinylbenzene 0.1 copy and benzoyl peroxide 170 copies of water which dissolved 0.1 copy of polyvinyl alcohol partial

saponification thing in the 1.7-copy above-mentioned mixed solution was added, and it was considered as suspension dispersion liquid. The above-mentioned suspension dispersion liquid were added to the reactor which put in and carried out the nitrogen purge of 15 copies of water, and it was made to react to it with the reaction temperature of 70–95 ** for 6 hours. It dried and dried and after ending reaction and a ** exception obtained the constituent (E) of the styrene acrylic acid 2-ethyl *****-** laine acid monobutyl copolymer. 15 copies and Tg were 60 **, the molecular weight distribution of the obtained resin had [about 32,000] a shoulder for the peak in the position of 06500, and the THF insoluble matter was [acid value] 0.3.

[0277]Examples 9–12 are examples concerning this invention 3.

[0278]Resin composition (A) of example 9 and the synthetic example 1 Magnetic oxide of iron of 100 copy and the example 1 of manufacture 100 copy and negative charge controlling agent (monoazo color system chromium complex) One copy and low molecular weight polypropylene It is made to be the same as that of Example 1 using the three-copy above-mentioned material. The negative triboelectric charging magnetic toner of 6.8 micrometers (0.2% of content of a magnetic toner particle with a particle diameter of 12.7 micrometers) of weight average particle sizes (D_4) was obtained.

[0279]1.2 copies of hydrophobic silica pulverized coal processed by silicone oil after carrying out hexamethyldisilazane treatment were mixed with 100 copies of this magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0280]Several multi-sheet image output test up to 6000 sheets was done like Example 1 using this magnetic developer. A result is shown in Table 7.

[0281]It blended as combination of the material of ten to example 12 toner was shown in Table 6, and also the toner was manufactured like Example 1, respectively, and it evaluated like Example 1. A result is shown in Table 7.

[0282]The toner shown above did not have weld with a device wall in the grinding process at the time of manufacture, either, and was good grindability. (However, it was satisfactory, especially although the time which grinding takes with the toner of Example 11 since the diameter of a crushed grain is minute was the longest and dirt was faintly seen by the grinder collision plate) A picture characteristic, fixability, offset-proof nature, and blocking resistance showed the very good result as they were shown in Table 7.

[0283]

[Table 6]

	実施例9	実施例10	実施例11	実施例12
<内添配合> (部)				
磁性酸化鉄	製造例1 100	製造例2 100	製造例3 100	製造例4 100
結着樹脂	(A) 100	(B) 70	(C) 120	(D) 90
モノアゾ染料系 クロム錯体	1	1	1	1
ポリプロピレン ワックス	3	3	3	3
<外添配合> (部)				
トナー	100	100	100	100
疎水性シリカ	1.2	0.6	1.6	0.4
<粒度分布>				
D ₄	6.8 μ m	11.0 μ m	4.0 μ m	8.0 μ m
12.7 μ m以下の 粒子の体積	0.2 %	33 %	0 %	4.3 %

The magnetic oxide of iron of the example 1 of comparative example 6 comparison manufacture and the resin composition E of the example 1 of comparison composition were used, and also the toner was manufactured like Example 1, and the same evaluation as Example 1 was performed. In the grinding process at the time of toner production, the throughput per time was falling about 20% as compared with Example 9, and when it investigated the collision plate of the grinder, the toner composition was welding it a little. Compared with the example, it was inferior and was an insufficient result as the result of other evaluations was also shown in Table 7.

[0284]

[Table 7]

試験項目	画 像 濃 度		カブリ ドット再現性		耐オフセット性		耐プロツキシング性		粉碎時粉砕機衝突板の融着	
	常温常温初期	常温常温6000枚後	高温高温6000枚後	低温低温6000枚後	常温常温3000枚時	低温低温3000枚時	定着性	耐オフセット性	耐プロツキシング性	粉碎時粉砕機衝突板の融着
実施例 9	1.44	1.46	1.40	1.46	1.2%	○	○	○	○	△
実施例 10	1.45	1.45	1.42	1.46	1.0%	○△	○	○△	○	△
実施例 11	1.46	1.44	1.38	1.42	1.4%	○	△	△	○	△
実施例 12	1.44	1.46	1.42	1.43	1.1%	○	△	○	○	△
比較例 6	1.40	1.15	1.05	1.21	5.3%	×	△	△	△	△

The physical properties of the toner of Examples 9–12 and the comparative example 6 are shown in the following table 8.

[0285]

[Table 8]

	トナー		
	THF 不溶分	Ms/Ma	Ms ₂ /Ma ₂
実施例 9	35部	1.8	3.0
実施例 10	45部	1.4	3.6
実施例 11	40部	1.4	12.5
実施例 12	50部	2.2	11.8
比較例 6	10部	3.7	3.4

Examples 13–16 are examples concerning this invention 4.

[0286] Example 13 and styrene 2-ethylhexyl acrylate 100 copies Maleic acid n-butyl half ester copolymer (the copolymerization weight ratio 7.5:1.5:1, Mw300,000)

– Magnetic oxide of iron of the example 1 of manufacture One copy of 100 copy and negative charge controlling agent (dialkyl-salicylic-acid system chromium complex), and low molecular weight polypropylene It is made to be the same as that of Example 1 using the four-copy above-mentioned material. The negative triboelectric charging magnetic toner of 7.0 micrometers (5% of content of a magnetic toner particle with a particle diameter of 12.7 micrometers) of weight average particle sizes (D_4) was obtained.

[0287] 1.2 copies of hydrophobic silica pulverized coal processed by silicone oil after carrying out hexamethyldisilazane treatment were mixed with 100 copies of this magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0288] The transfer device like drawing 9 was built into the device unit portion (toner cartridge) of laser beam printer LBP-8II (made by Canon, Inc.) of marketing of the obtained developer, and as shown in drawing 11, it converted. As conditions for the transfer roller 16, it was considered as the surface rubber hardness of 27 degrees of a transfer roller, transfer current 1 microA, and the contact pressure 50 [g/cm].

[0289] Revolving speed of the outer diameter of the photoconductive drum 3 which is process speed is set to sec in 100 mm /, Primary charging is -700V and a gap (300 micrometers) is set as non-contact for the developer layer on a photoconductive drum and a developing sleeve (magnet intension 15), Impressing AC bias ($f= 1,800$ Hz, $V_{pp}=1,600$ V) and DC bias ($V_{DC}=-500$ V) to a developing sleeve, V_L was set to -170V and image output was performed. The result of image output having been carried out and having evaluated the toner fixed image by which heat pressing roller fixing was carried out is shown in Table 9.

[0290] The magnetic toner of 13 micrometers (40% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes was obtained like Example 1 except using the magnetic oxide of iron of the example 2 of example 14 manufacture.

[0291] 0.8 copy of hydrophobic colloidal silica processed by silicone oil was mixed with 100 copies of obtained magnetic toner with the Henschel mixer, and the magnetic developer was prepared. The image output test was done like Example 13 except setting process speed to sec in 250 mm /using the prepared magnetic developer. A result is shown in Table 9.

[0292] The image output test was done like Example 13 except having set example 15 transfer condition to 20 [g/cm]. A result is shown in Table 9.

[0293] The magnetic toner of 4 micrometers (0% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes (D_4) was obtained like Example 1 except making the magnetic oxide of iron of the example 3 of example 16 manufacture into 80 copies.

[0294] 1.8 copies of hydrophobic colloidal silica processed by silicone oil was mixed with 100

copies of obtained magnetic toner with the Henschel mixer, and the magnetic developer was prepared.

[0295]The image output test was done like Example 13 except setting process speed to sec in 36 mm /using this magnetic developer. A result is shown in Table 9.

[0296]Except for using the magnetic oxide of iron of the example 1 of comparative example 7 comparison manufacture, the magnetic toner of 10 micrometers (27% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes was obtained like Example 1. The image output test was done like Example 13 using the magnetic developer which prepared and prepared the magnetic developer like Example 13 using the obtained magnetic toner. A result is shown in Table 9.

[0297]Except for using the magnetic oxide of iron of the example 2 of comparative example 8 comparison manufacture, the magnetic toner of 7 micrometers (0.3% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes was obtained like Example 1. The image output test was done like Example 14 using the magnetic developer which prepared and prepared the magnetic developer like Example 14 using the obtained magnetic toner. A result is shown in Table 9.

[0298]The magnetic oxide of iron of the example 1 of comparative example 9 manufacture was used, the magnetic toner which has 14 micrometers (60% of content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers) of weight average particle sizes like Example 1 was obtained, the magnetic developer was prepared like Example 13, and the image output test was done like Example 13. A result is shown in Table 9.

[0299]As compared with the magnetic developer of Example 13, dot reproducibility was inferior and TOBICHIRI of the toner was also seen.

[0300]

[Table 9]

	画像濃度	転写状態	紙搬送状態	画像品質	カブリ
実施例13	○	○	○	○	○
実施例14	○	○	○	○	○
実施例15	○	○	△	○	○
実施例16	○	○	○	○	○
比較例1	△	×	○	×	×
比較例2	△	×	○	△	×
比較例3	○	○	○	×	○

(1) image concentration: -- usual 3,000 sheets of regular paper (75 g/m^2) copy for LBP -- the image concentration maintenance at the time of paper estimated.

[0301]

○ (Good) More than :1.35** (good) : -- or less [1.0 – 1.34x(improper):] 1.0 (2) transfer-state: -- usual 3,000 sheets of regular paper (75 g/m^2) copy for LBP -- the pasteboard of $120\text{g}/\text{m}^2$ severe as a transfer condition was ***(ed) after paper, and the transfer omission state estimated.

[0302]

○ : fitness (refer to drawing 8 a)

**: Practical-use good x: Defect (refer to drawing 8 b)

(3) paper carrying state: -- the thin paper of 50 g/m^2 -- a 1,000-sheet copy -- paper was carried out and the generation state of unjust conveyances, such as bias, was evaluated.

[0303]

O : -- 1 time less than/1,000 sheet **:2 to 4 times [/1,000 sheets] x:5 times more than/1,000-sheets (4) imaging quality; -- usual 3,000 sheets of regular paper (75 g/m^2) copy for LBP -- viewing estimated spilling of the toner of a picture, a husky part, etc. at the time of paper.

[0304]

O :fitness **:practical use good x:practical use improper (5) fogging: -- the bottom of low-humidity/temperature environment (10 **, 15%RH) -- 3,000 sheets of regular paper ($75\text{g}/\text{m}^2$) copy for LBP -- fogging at the time of paper was measured and evaluated.

[0305]

O (Good) :2.0%or less ** (good) More than :2.0–5.0% x (improper):5.0% [0306]

[Effect of the Invention]In this invention, it is 13.5 micrometers or less of weight average particle sizes, and the content of a magnetic toner particle with a particle diameter of not less than 12.7 micrometers uses the magnetic oxide of iron which has the feature in distribution of a silicon element as a magnetic body of magnetic toner with many 50 or less % of the weight of magnetic toner particles with fine particle diameter.

Therefore, the environmental stability and the developing characteristic of magnetic toner can be raised.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a figure showing the dissolution curve of a magnetic oxide of iron.

[Drawing 2]It is a mimetic diagram of magnetic-oxide-of-iron particles for explaining distribution of a silicon compound.

[Drawing 3]It is a schematic diagram about one example of the image forming device (elastic blade possession) used for this invention.

[Drawing 4]It is a rough explanatory view showing one example of the image forming device (elastic blade possession) used for this invention.

[Drawing 5]It is a rough explanatory view showing one example of the device unit used for this invention.

[Drawing 6]It is a block diagram showing one example of the facsimile machine of this invention.

[Drawing 7]It is an explanatory view of the checkered pattern for examining the developing characteristic of magnetic toner.

[Drawing 8]It is a figure showing the toner image after transfer typically.

[Drawing 9]It is an explanatory view of a roller type transfer device.

[Drawing 10]It is an explanatory view of a belt type transfer device.

[Drawing 11]It is a rough explanatory view showing other examples of the device unit used for this invention.

[Description of Notations]

- 1 Developer
- 2 Developer container
- 3 Latent image support
- 4 Transfer means
- 5 A laser beam or analog light
- 6 Developing sleeve
- 7 Heat pressing fixing means
- 8 Cleaning blade
- 9 Elastic blade
- 11 Electrifying device
- 12 Bias applying means
- 13 Magnetic developer
- 14 Cleaning means
- 15 Magnetic field generating means
- 19 IRESU exposure

[Translation done.]

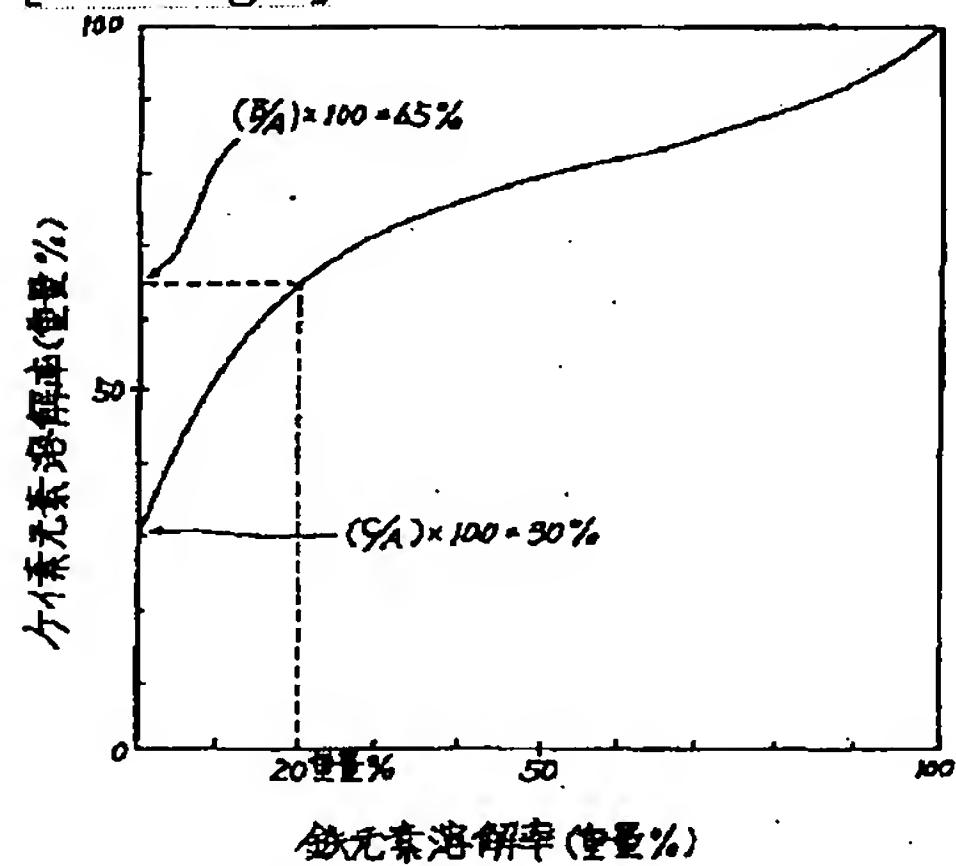
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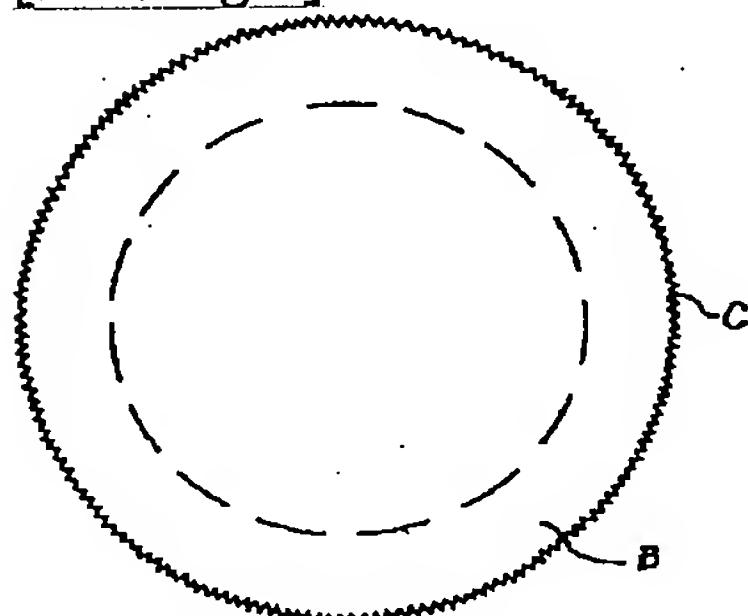
DRAWINGS

[Drawing 1]

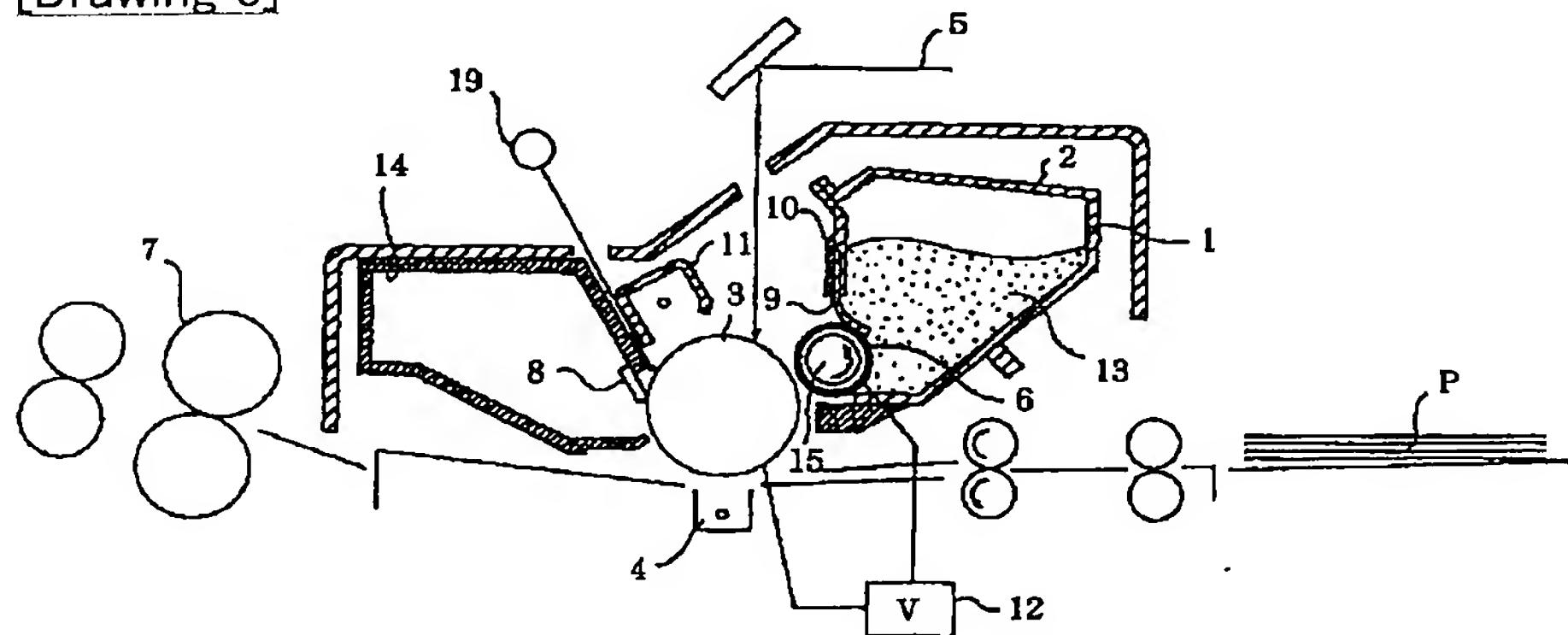


製造例1の磁柱酸化鉄の溶解曲線

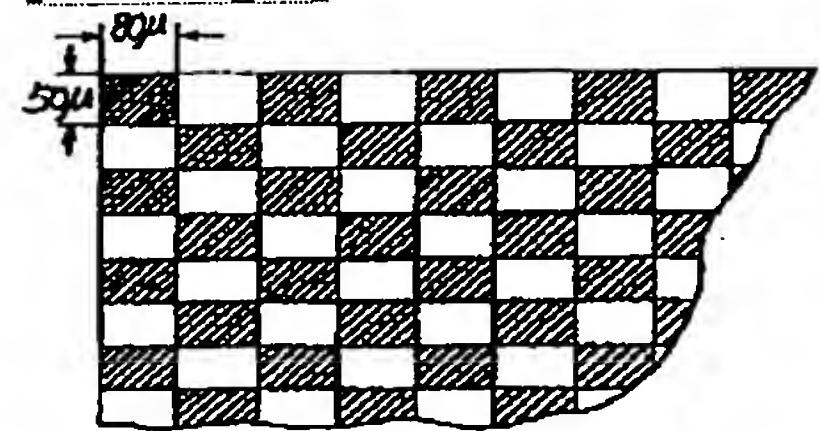
[Drawing 2]



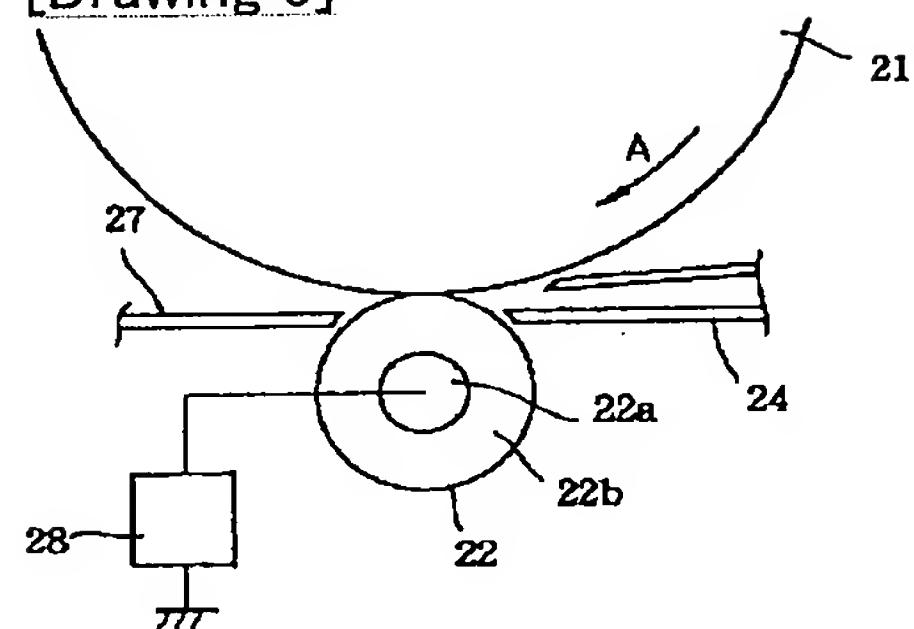
[Drawing 3]



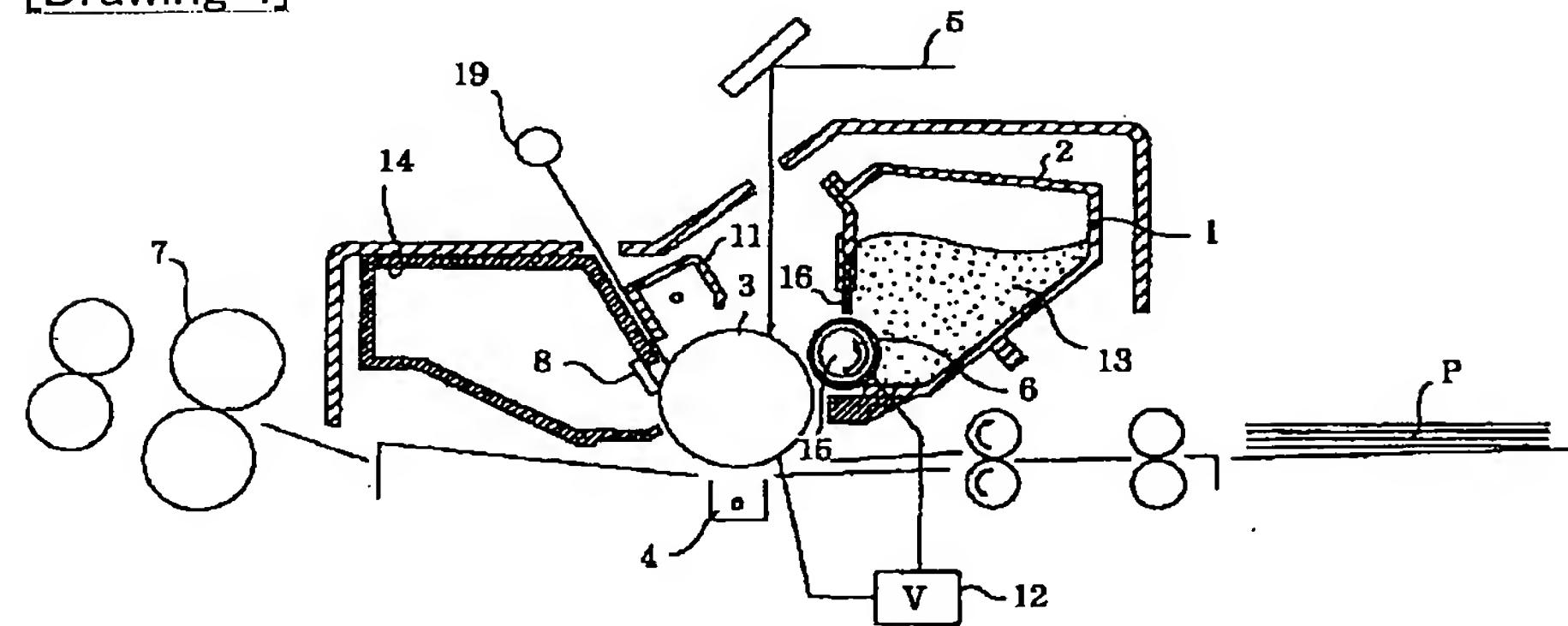
[Drawing 7]



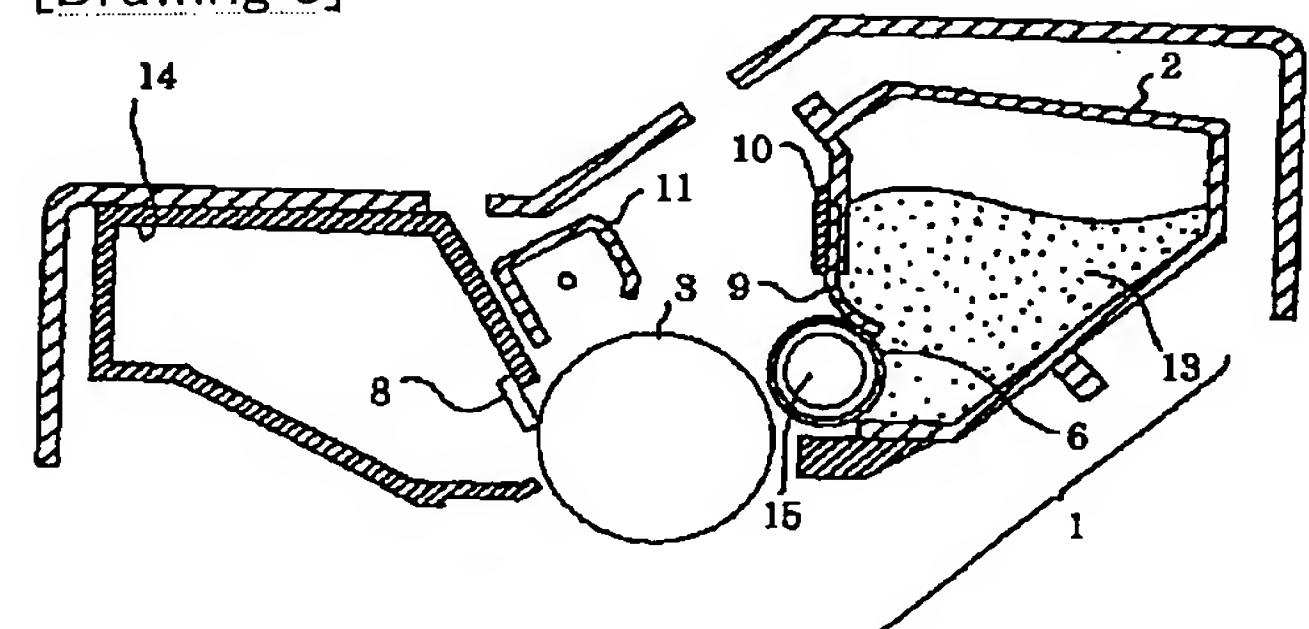
[Drawing 9]



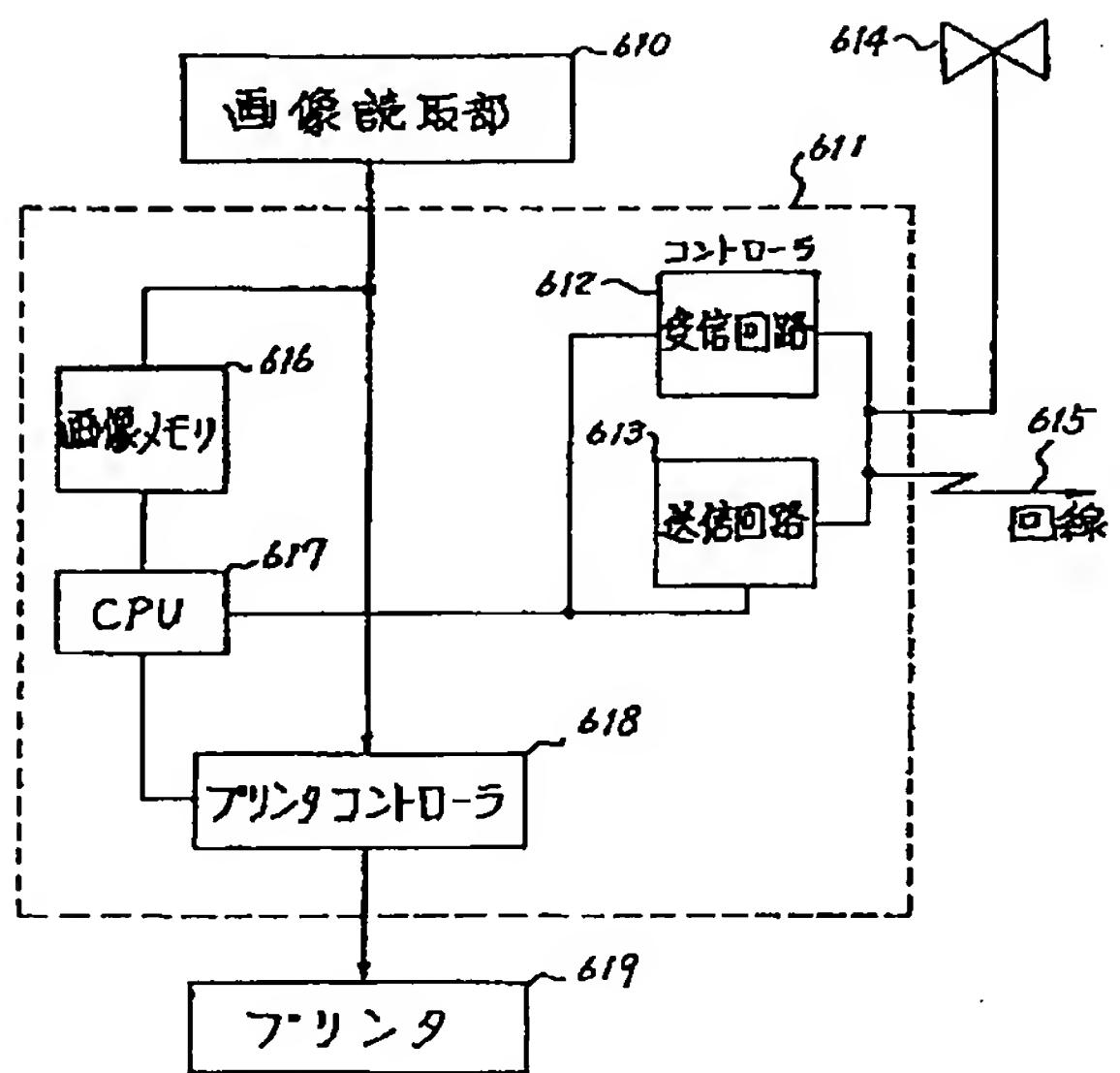
[Drawing 4]



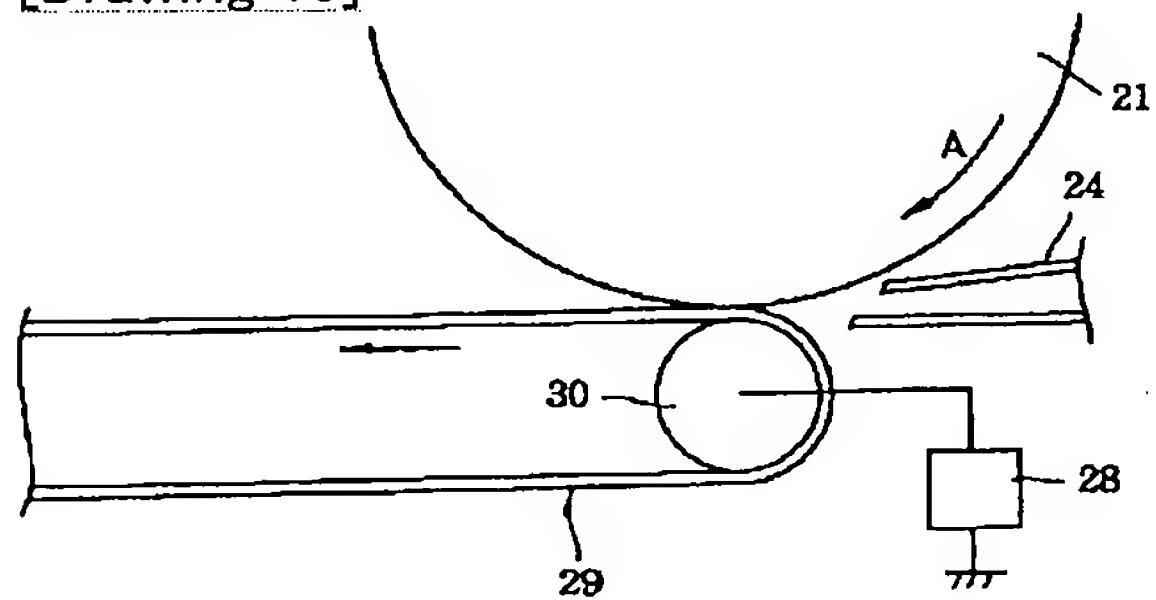
[Drawing 5]



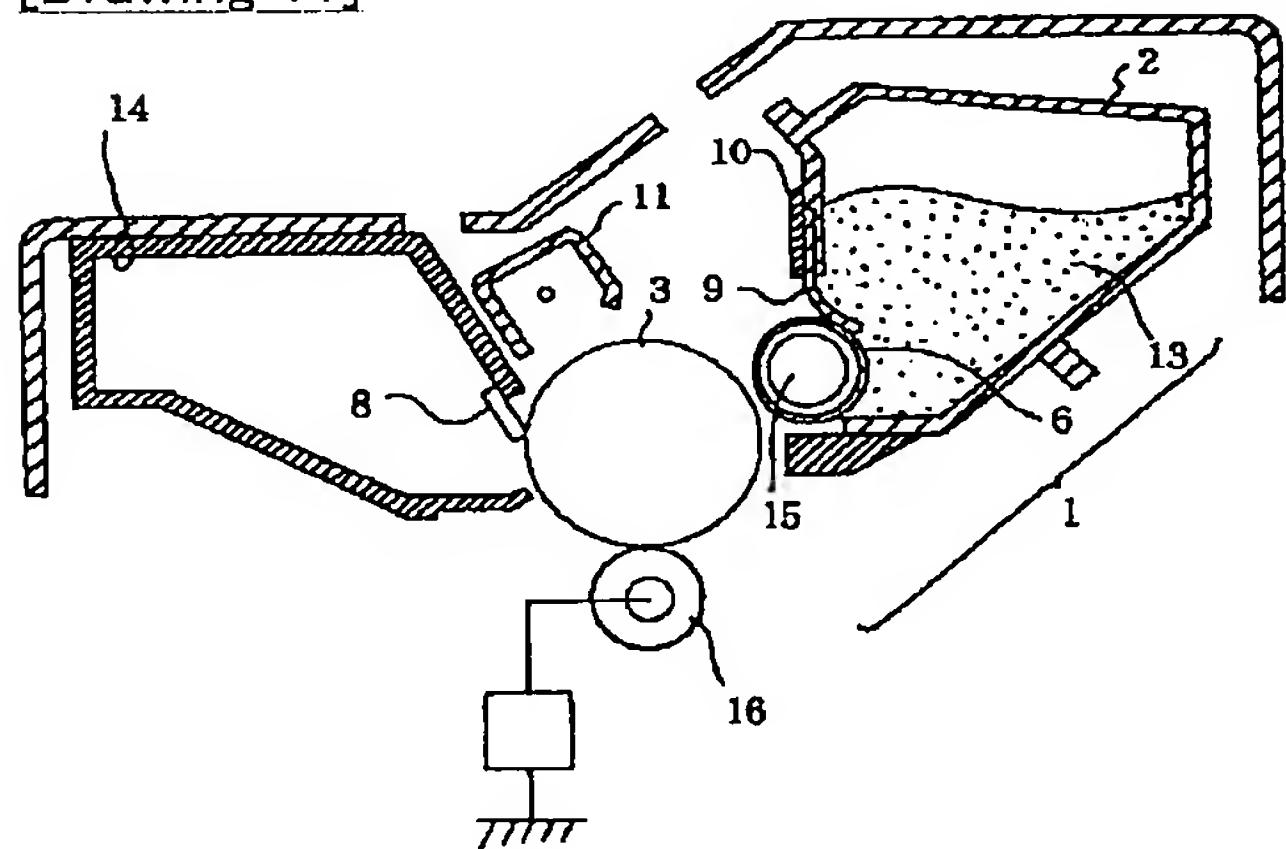
[Drawing 6]



[Drawing 10]

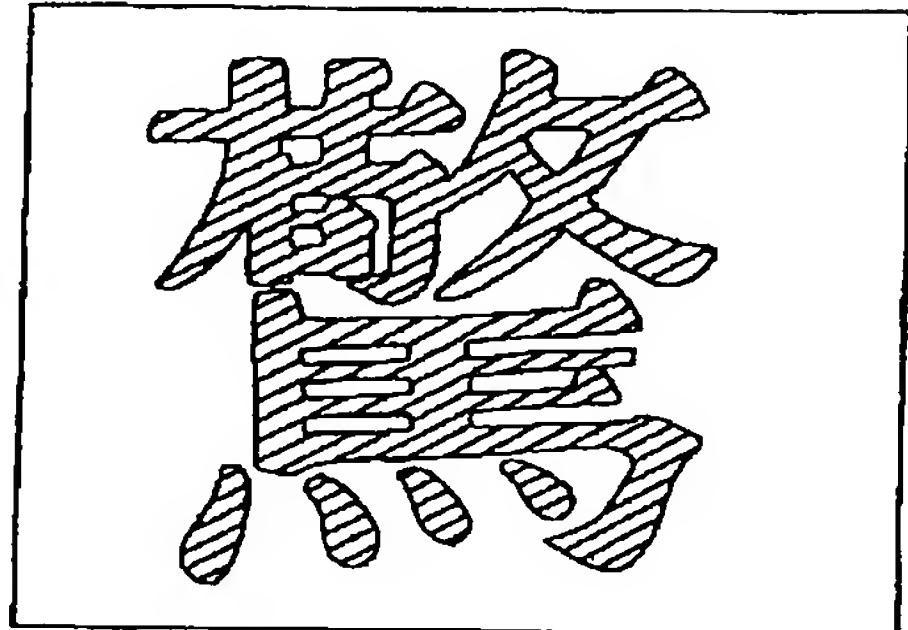


[Drawing 11]

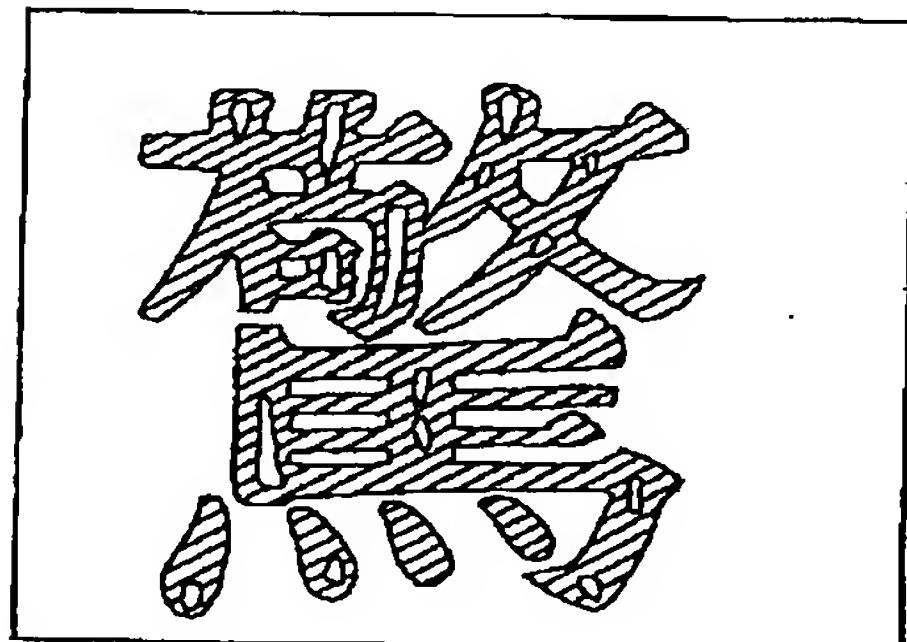


[Drawing 8]

(a)



(b)



[Translation done.]

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(54)【発明の名称】 磁性トナー及び画像形成方法

(57)【要約】

【目的】 本発明は、環境安定性に優れており、長期間にわたる耐久においても画像濃度の高いトナー画像を形成し得、ドット再現性、定着性及び耐オフセット性の優れている磁性トナーを提供することを目的とする。

【構成】 本発明は、重積平均粒径が13.5ミクロン以下であり、粒径12.7ミクロン以上の磁性トナーラジ子の含有量が50重量%以下である磁性トナーに含まれる磁性酸化鉄として、該磁性酸化鉄のケイ素元素の含有率が、鉄元素を基準として0.5~4重量%であり、該磁性酸化鉄の鉄元素溶解率が20重量%までに存在するケイ素元素の含有量Bと、該磁性酸化鉄のケイ素元素の全含有量Aとの比(B/A)×100が44~84%であり、該磁性酸化鉄の表面に存在するケイ素元素の含有量Cと該含有量Aとの比(C/A)×100が10~55%であるものを使用している。

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(4)

特開平6 194869

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表面とトナー像とが溶融状態で加圧下で接触するためにトナー像の一部が定着ローラー表面に付着・転移し、次の被定着シートにこれが再転移していわゆるオフセット現象を生じ、被定着シートを汚すことがある。熱定着ローラー表面に対してトナーが付着しないようにすることは熱ローラー定着方式の必須条件の一つとされている。

【0015】従来、定着ローラー表面にトナーを付着させない目的で、例えば、ローラー表面をトナーに対して離型性の優れた材料、シリコンゴムや非素系樹脂などで形成し、更にその表面にオフセット防止及びローラー表面の疲労を防止するためにシリコーンオイルの如き離型性の良い液体の薄膜でローラー表面を被覆することが行なわれている。しかしながら、この方法はトナーのオフセットを防止する点では極めて有効であるが、オフセット防止用液体を供給するための装置が必要なため、定着装置が複雑になること等の問題点を有している。それゆえ、オフセット防止用液体の供給によってオフセットを防止する方向は好ましくなく、むしろ定着温度領域の広い耐オフセット性の高いトナーの開発が望まれているのが現状である。そこでトナーとして離型性を増すために加熱時に充分溶融するような低分子量ポリエチレン、ポリプロピレン等のワックスを添加する方法も行なわれているが、オフセット防止には有効である反面、トナーの凝集性が増し、帶電特性が不安定となり、耐久性の低下を招き易い。そこで他の方法としてバインダー樹脂に改良を加える工夫がいろいろと試みられている。

【0016】例えば、トナー中のバインダー樹脂のガラス転移温度(T_g)や分子量を高めトナーの溶融粘弹性を向上させる方法も知られている。しかしながら、このような方法は、オフセット現象を改善した場合、定着性が不十分となり、高速現像化や省エネルギー化において要求される低温度下での定着性即ち低温定着性が劣るという問題が生じる。

【0017】一般に、トナーの低温定着性を改良するには、溶融時におけるトナーの粘度を低下させ、定着基材との接着面積を大きくする必要があり、このために使用するバインダー樹脂の T_g や分子量を低くすることが要求される。

【0018】バインダーの T_g を低下させるとトナーが高温下でブロッキングし易くなり、保存安定性にかかわる。

【0019】特に、近年の複写機やレーザービームプリンターの小型化に伴い定着器、電装部等の熱源がクリーナーや現像器に非常に接近するため最低限50°Cにおける耐ブロッキング性の確保が必要となってきている。

【0020】即ち低温定着性と耐ブロッキング性及びオフセット防止性を同時に満足することは非常に困難であった。

【0021】この問題を解消するのに、特開昭56-16043号公報では反応性ポリエステル樹脂の存在下

でビニル系单量体を重合し、重合の過程で架橋反応、付加反応、グラフト化反応を介して高分子化させた樹脂を用いたトナーが提案されているが、低温定着性、オフセット防止性の点で互いの樹脂の機能を充分に生かすことができない。

【0022】さらに、磁性成分現像剤に用いた場合には、磁性酸化鉄の分散が不均一になりやすい。

【0023】また単純にポリエステル樹脂とゲルコンテントが異なる2種類(ゲル化度80%以上とゲル化度10%未満)のビニル系樹脂をブレンドした樹脂を用いたトナーが特公平1-15083号公報で提案されているが、このものは低温定着性については良いものの、一成分磁性現像剤に用いた場合には磁性酸化鉄の分散が不均一になりやすい。

【0024】このようにビニル系重合体とポリエステル樹脂を混合して接着樹脂として用いる系では2種類の異なる物性を有する樹脂を用いるととから、樹脂中への着色剤等のトナー構成物質の分散が均一・粗い樹脂を用いる場合に比較して不均一になりやすい。特に、ジャンピング現像に用いられる一成分トナーにおいては、磁性体の分散が不均一になった場合にカブリやトナーの飛び散り発生によるドット再現性の悪化が目立つ傾向があり、さらに數千枚に渡る画出し試験においては濃度低下が目立ち実用上好ましくない。つまり、ビニル系重合体とポリエステル樹脂を混合して一成分磁性トナーに用いる場合、定着性、オフセット性及び画像品質を同時に満足することは未だ達成されていない。

【0025】また近年、複写機及びレーザービームプリンターのとき電子写真技術を用いた画像形成装置の機能が多様化し、一層トナー画像の高精細化、高画質化が求められているが、きわめて微細な潜像に至るまでつぶれたりとされたりすることなく忠実に再現するためには、特開平1-112253号公報で提案されているように、トナー粒子を小粒径化することが有効である。しかしトナーの粒径を小さくしようとする程、粉碎工程における粉碎機内壁へのトナー組成物の附着の発生等による粉碎効率の低下や前述のような様々な弊害を生じやすい。

【0026】また、トナー粒径が小さくなる程、トナーの流動性は低下するため、トナーの流動性維持のために多量の無機微粉体を添加すると、容易に流動性を向上させることが可能であるが、感光体を損傷する原因となり、感光体へのトナーの附着、フィルミング等を発生しやすくなり、トナー飛散等も悪化する。

【0027】他に、近年の急速な事務の合理化に伴い、短時間に大量のコピーあるいはプリントアウトできる画像形成方法が望まれているが、潜像保持体の外径の回転速度の比較的速い画像形成方法においては、出力される画像が輪郭部のみの画像となる「転写巾抜け」とよばれる転写不良が生じやすい問題もある。

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ンカップリング剤で処理されたシリカ微粉体とシリコーンオイルとをヘンシェルミキサー等の混合機を用いて直接混合しても良いし、ベースとなるシリカヘシリコーンオイルを噴射する方法によても良い。あるいは適当な溶剤にシリコーンオイルを溶解あるいは分散せしめた後、ベースのシリカ微粉体とを混合し、溶剤を除去して作製しても良い。

【0160】本発明中の磁性トナーには、必要に応じてシリカ微粉体以外の外部添加剤を添加してもよい。

【0161】例えば帶電補助剤、導電性付与剤、流動性付与剤、ケーリング防止剤、熱ロール定着時の離型剤、滑剤、研磨剤等の働きをする樹脂微粒子や無機微粒子である。

【0162】磁性トナーと混合される無機微粉体または疎水性無機微粉体は、磁性トナー100重量部に対して0.1~5重量部(好ましくは0.1~3重量部)を使用するのが良い。

【0163】本発明に係る静電荷像を現像するための磁性トナーを作製するには磁性粉及びビニル系、非ビニル系の熱可塑性樹脂、必要に応じて着色剤としての顔料又は染料、荷電制御剤、その他の添加剤等をポールミルの如き混合機により充分混合してから加熱ロール、ニーダー、エクストルーダーの如き熱混練機を用いて熔融、捏和及び練りして樹脂類を互いに相溶せしめた中に顔料又は染料を分散又は溶解せしめ、冷却固化後粉碎及び厳密な分級をおこなって本発明に係るところの磁性トナーを得ることが出来る。

【0164】本発明に係るケイ素元素を有する磁性酸化鉄は、例えば下記方法で製造される。

【0165】第一鉄塩水溶液に所定量のケイ酸化合物を添加した後に、鉄成分に対して当量または当量以上の水酸化ナトリウムの如きアルカリを加え、水酸化第一鉄を含む水溶液を調製する。調製した水溶液のpHをpH7以上(好ましくはpH8~10)に維持しながら空気を吹き込み、水溶液を70℃以上に加温しながら水酸化第一鉄の酸化反応をおこない、磁性酸化鉄粒子の芯となる種晶をまず生成する。

【0166】次に、種晶を含むスラリー状の液に前に加えたアルカリの添加量を基準として約1当量の硫酸第一鉄を含む水溶液を加える。液のpHを8~10に維持しながら空気を吹込みながら水酸化第一鉄の反応をすすめ種晶を芯にして磁性酸化鉄粒子を成長させる。酸化反応がすすむにつれて液のpHは酸性側に移行していくが、液のpHは6未満にしない方が好ましい。酸化反応の終期に液のpHを調整することにより、磁性酸化鉄粒子の表面および表面にケイ酸化合物を所定量偏在させることが好ましい。

【0167】添加に用いるケイ酸化合物は、市販のケイ酸ソーダ等のケイ酸塩類、加水分解等で生じるゾル状ケイ酸等のケイ酸が例示される。尚、本発明に悪影響を与

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えない限り硫酸アルミニウム、アルミニウム等のその他添加剤を加えても良い。

【0168】第一鉄塩としては、一般的に硫酸法チタン製造に副生する硫酸鉄、鋼板の表面洗浄に伴って副生する硫酸鉄の利用が可能であり、更に塩化鉄等が可能である。

【0169】水溶液法による磁性酸化鉄の製造方法は一般に反応時の粘度の上昇を防ぐこと、及び、硫酸鉄の溶解度から鉄濃度0.5~2mol/lが用いられる。硫酸鉄の濃度は一般に薄いほど製品の粒度が細くなる傾向を有する。又、反応に際しては、空気量が多い程、そして反応温度が低いほど微粒化しやすい。

【0170】上述の製造方法により、透過電顕写真による観察で、ケイ酸成分を有する磁性酸化鉄粒子が、主に板状面を有さない曲面で形成された球形状粒子から構成され、八面体粒子を殆ど含まない磁性酸化鉄を生成し、その磁性酸化鉄をトナーに使用することが好ましい。

【0171】本発明の磁性トナーを使用するための画像形成装置、装置ユニット及びファクシミリ装置について説明する。

【0172】画像形成装置の好ましい一具体例を図3を参照しながら説明する。

【0173】一次帯電器11でOPC感光体3表面を負極性に帯電し、レーザ光による露光5によりイメージキャピングによりデジタル潜像を形成し、カウンター方向に設置されたウレタンゴム性の弹性ブレード8および磁石15を内包している現像スリーブ6を具備する現像装置1の磁性トナーを有する一成分系磁性現像剤13で該潜像を反转現像する。現像部において感光ドラム3の導電性基体と現像スリーブ6との間で、バイアス印加手段12により交互バイアス、パルスバイアス及び/又は直流バイアスが印加されている。転写紙Pが搬送されて、転写部にくると静電的転写手段4により転写紙Pの背面(感光ドラム側と反対面)からコロナ帯電することにより、感光ドラム表面上の現像潜像(トナー像)が転写紙P上へ静電転写される。感光ドラム3から分離された転写紙Pは、加熱加圧ローラ定着器7により転写紙P上のトナー画像を定着するために定着処理される。

【0174】転写工程後の感光ドラムに残留する一成分系現像剤は、クリーニングブレード8を有するクリーニング器14で除去される。クリーニング後の感光ドラム3は、イレース露光19により除電され、再度、一次帯電器1による帯電工程から始まる工程が繰り返される。

【0175】静電荷像保持体(感光ドラム)は感光層及び導電性基体を有し、矢印方向に動く。トナー担持体である非磁性円筒の現像スリーブ6は、現像部において静電荷保持体表面と同方向に進むように回転する。非磁性円筒の現像スリーブ6の内部には、磁界発生手段である多極永久磁石15(マグネットロール)が回転しない上